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Editors

Materials for Construction and Civil Engineering

Science, Processing, and Design

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The translation from Portuguese to English was supported by the Program 'Alberto Lacerda 2013' | Luso-American Foundation.

ISBN 978-3-319-08235-6 ISBN 978-3-319-08236-3 (eBook)
DOI 10.1007/978-3-319-08236-3
Springer Cham Heidelberg New York Dordrecht London

Library of Congress Control Number: 2014955473

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Printed on acid-free paper

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Preface

The current economic panorama has been particularly adverse for the architecture and civil engineering sectors. We firmly believe that the innovation and development of new materials with enhanced and/or innovative properties will bring about the opportunity of restoring these sectors.

However, the remarkable multiplicity and diversity of materials currently available in civil engineering put designers, architects, and civil engineers in a problem of growing complexity—the *selection of materials*.

The selection of materials in civil engineering can be based, naturally, on features such as suitability, cost, life cycle, and the materials recyclability. Nevertheless, the future of civil engineering lies in the higher value-added materials. Hence, the selection of materials for a certain project is an iterative task, where the optimization of solutions can only be obtained through the dialogue between the project's specialists, architectures, and civil and materials engineers.

Naturally, for such discussion to be possible, it is imperative that all the actors dominate the same technical language and share a set of scientific knowledge, which will allow for communication and optimized solutions.

The present work is intended to contribute to that platform of specialists that is committed to the civil engineer/architecture project. We intend to offer its readers information regarding the main groups of materials used in civil construction, highlighting the nomenclature, properties, fabrication processes, selection criteria, products/applications, life cycle and recyclability, and even normalization.

This book is the result of extensive work in a broad spectrum of subjects and competences in the areas of materials and civil engineering, as well as architecture. In its foundation there is a multidisciplinary team of several specialists of distinct Portuguese institutions, such as LNEC, CTCV, ISEL, LNEG, and IST. Despite the scientific edition of the work, it certainly reflects some level of heterogeneity in the approach chosen by each author.

Chapters 1–5 include the structural and more traditional materials in civil engineering—hydraulic binders, bituminous materials, concrete, plastering, and renders; Chaps. 6–9 comprise structural materials and/or finishing materials like steel, ceramic, glass, ornamental stones, polymers, and polymer matrix composites; Chaps. 12 and 13 depict the natural materials such as wood and cork; in Chap. 14 we introduce nanomaterials; Chaps. 15 explain the corrosion phenomena and its control; Chap. 16 introduces structural adhesives, while the main properties and the uses of paints and organic coatings are presented in Chap. 17. Chapter 18 presents the life cycle of the different products, as well as the integrated waste management of; and Chap. 19 concludes the book with the regulation and certification of construction products. To the authors, we publicly express our sincere thanks for their contribution, without which this book would not be possible. Thanks to the first publisher, “ISTPress” the IST academic publisher, since day one. Very special thanks to Springer, for its recognition and commitment on the publication of the book.

Lisbon, Portugal
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Glossary

A

Abrasion resistance (Plaster; render) Wear resistance of the surface of a hardened mortar by mechanical action

Abrasive (Ornamental stone) Generic designation of hard and wear-resistant substances used to wear and polish

Acid rock (Ornamental stone) Igneous rock with more than 66 wt% silica

Addition (Plaster; render; concrete) Finely divided inorganic material, which can be added to the matrix (mortar, concrete, and others) with the purpose to obtain or improve specific properties

Additive (Polymeric matrix composites; organic coatings; structural adhesives; polymer) Substance added in small quantities to a formulation (adhesive, polymer resin, paints, varnishes, etc.) with the purpose of improving or modifying the processability (plasticizers, lubricants, stabilizers, release agents, etc.), the external appearance (colors, pigments, etc.), the performance (antioxidants, protection to ultraviolet radiation, the antistatic flame retardants, foams, etc.), or the recycling processes (stabilizers, additives repairers, etc.)

Adherence (Plaster; render) Maximum breaking force per unit area of a mortar applied on a support, which can be determined by applying a tensile force or shearing

Adherence (Organic coatings) Property of a film used to evaluate the set of binding forces that develop between that film and the substrate where it is applied

Adhesion (Organic coatings) Property of a film, resulting from the binding forces developed between the film and the substrate on which it is applied

Adhesion (Structural adhesives) Phenomenon by which two surfaces are held together by chemical, physical, or physicochemical forces resulting from the presence of an adhesive [NP 3672:1990]

Adhesive (Structural adhesives) Product able to maintain in a state of adhesion of two surfaces of one or more identical or different materials [NP 3672:1990]

Adhesive failure (Plaster; render) Rupture that occurs at the interface between the mortar and the support, or generally at the interface between the adhesive and either glued surfaces

Adhesiveness (Structural adhesives) Capacity of a material to produce adhesion

Adhesives (Structural adhesives; polymer) Formulations usually involving polymer, used to bind two or more surfaces together, providing a certain strength to this union. Divided into adhesives of thermal, contact, and structural application. Nonmetallic substance capable of joining materials by surface bonding (adhesion), and the bond possessing adequate internal strength (cohesion) [EN923:2005 + A1:2008]

Admixture (Render; plaster; concrete; polymer) Denomination given to additions used in small amounts (<4 wt%; <5 % per cement weight in concrete) to improve specific properties of the final product (see additives)

Agglomerate (Cork) Material obtained by agglomeration of granules (expanded or not expanded) or possibly regranulates

Aggregate (Concrete and binders; Bituminous materials) Natural, artificial, reclaimed, or recycled granular mineral materials used in construction

Air-entraining agent (Plasters; Stucco) Admixture that allows the incorporation of a controlled amount of air bubbles distributed uniformly throughout the mortar, which remain after hardening

Alkyd resin (Polymer) Alkyd resins ("al" as alcohol and "id" as acid) are made from esters of unsaturated carboxylic acids and polyhydric alcohols; polymerization by radical attack to double links produces a coating (see *resin*)

Alternating copolymer (Polymer) Copolymer wherein the constituent monomers are alternately distributed in the chain (see *copolymer*)

Anion (Corrosion) Negatively charged ion (e.g., Cl^- or OH^-)

Annual ring (or Annual growth ring) (Wood) Cross section of a tree growth layer, or part thereof, corresponding to the wood produced in a year

Anode (Corrosion) Electrode where an oxidation reaction occurs. This reaction may involve molecules or anions from the environment or the atoms of a metal (giving rise to positive ions or insoluble compounds)

Anodic current (Corrosion) Current caused by the occurrence of oxidation reaction

Anodic inhibitor (Corrosion) Inhibitor that interferes with the anodic reaction. Normally, these are anions that migrate to anode surfaces, forming protective film layers

Anodic protection (Corrosion) Protection against corrosion is obtained by increasing the electrode potential so as to achieve the material's passivation. It is only feasible if the material shows a passivation domain at the working pH

Anodizing (Corrosion) Corrosion protection method used in several metals in which the oxidation of the metal is promoted in order to obtain a thick layer of protective oxide

Antireflective glass (Glass) Glass with a surface coating that allows to minimize the light reflection component and maximize the transmitted component, so that transparency and visibility in transmission are optimized (class of coated glasses)

Arcade (Ornamental stone) Series of contiguous arches; dome

Atmospheric corrosion (Corrosion) Corrosion by exposure to the atmosphere, usually to outdoors (see corrosion)

B

Bands (Ornamental stone) Strips or risers for coping

Banister (Ornamental stone) Small column usually used in support railings and window sills

Bark (Wood) Generic term for all exterior tissues that involve the xylem

Basalt (Ornamental stone) Extrusive igneous rock of volcanic origin and usually very hard, whose color ranges from dark gray to black

Basic rock (Ornamental stone) Igneous rock containing silica between 45 and 52 wt%

Belly or womb (Cork) Suberous inside part of the cork tissue corresponding to the last annual growth that reproduces all the irregularities of the surface of the inner bark. It is located inside relatively to the tree

Beveled (Ornamental stone) Wedge-shaped edge of a slab, tile, or plaque obtained by a beveling operation

Bimetallic corrosion (Corrosion) See *galvanic corrosion*

Binder (Structural adhesives) Component of an adhesive that is primarily responsible for the adhesion [NP 3672:1990]

Binder (Hydraulic binders) Substances that harden independently and that bind other solid materials together conferring cohesion and resistance to the whole system

Binders (Polymer matrix composites) Materials (usually resinous) that help the fibers remain agglomerated, providing them with protection to degradation due to environmental agents and also promoting the adhesion between the fibers and the matrix

Biochemical rock (Ornamental stone) Sedimentary rock formed by sedimentation of organic deposits

Biological corrosion (Corrosion) Deterioration of a metal by corrosion processes which result, directly or indirectly, from the activity of living organisms. Biological corrosion is not in itself a type of corrosion, but is characterized by the intervention of living organisms (see *corrosion*)

Biopolymer (Polymer) Polymer of biological origin (produced by living beings) (see *polymer*)

Bitumen (Binders and bituminous materials) Organic, very viscous, almost nonvolatile material, adhesive and impervious to water, crude petroleum derivative or present in natural asphalt, completely or nearly completely soluble in toluene

Bitumen emulsion (Binders and bituminous materials) Fine dispersion of bitumen in water, performed with the aid of an emulsifier

Bituminous binder (Binders and bituminous materials) Adhesive material containing bitumen or natural asphalt, or a mixture of both

Bituminous mixture (Binders and bituminous materials) Mixture of stone, sand, with or without filler, and a bituminous hydrocarbonated binder. The following bituminous mixtures can be distinguished: (1) closed or dense, when the percentage of voids is equal to or lower than 5 wt% after applying and compacting (virtually impermeable); (2) semi-closed or semi-dense, when the percentage of voids in work is less than 15 wt% and higher than 5 wt%, after spreading and compacting; and (3) open, when the percentage of voids is greater than 15 wt% after spreading and compacting

Bituminous mortar (Binders and bituminous materials) Mixture of sand with bitumen (3–4 wt%). In Portugal, the percentage of bitumen is not previously defined (see *mortar*)

Blended cements (Hydraulic binders) (1) Cements in which the clinker is partially replaced with cementitious materials or minerals during the cement manufacturing process, or (2) cements blended with cementitious materials or minerals during the preparation of grout, mortar, or concrete (see cement)

Bleeding (Concrete) Particular case of segregation that corresponds to the rise of water to the top concrete's surface and can drag fine particles, namely cement

Block (Cork) Large piece with the shape of a rectangular parallelepiped comprising one or more elements bonded

Block copolymer (Polymer) Copolymer whose chain is constituted by a sequence of different blocks, each one being constituted by a homopolymer sub-chain (see *copolymer*)

Bond, adhesive joint (Structural adhesives) Union of two adjacent substrates by means of an adhesive [NP 3672:1990]

Bond strength (Structural adhesives) Force per surface unit necessary to bring an adhesive joint to the point of failure, with failure occurring in or near the plane of the bond-line [EN 923:2005 + A1:2008]

Bonding (Structural adhesives) Action of bond and the result of that action [NP 3672:1990]

Breccia (Ornamental stone) Sedimentary rock consisting of fragments of natural agglomeration, cemented together by calcite or silica

Brittle conchoidal fracture (Glass) Morphology of brittle fracture in vitreous material. In brittle conchoidal fracture the fracture surface is similar to a shell surface. In brittle fracture, the forming energy of a critical crack is much bigger than the crack's propagation energy

Bush hammering (Ornamental stone) Surface finishing process that consists of creating protrusions and depressions with a puncture from 4 to 25 teeth in conical or pyramidal shapes. The finish can be made manually or automatically using an especially designed device

Brushed (Ornamental stone) Finishing processed with steel brushes giving a brushed aspect to stone

C

Calcite (Ornamental stone) Mineral composed of calcium carbonate ($CaCO_3$)

Calibrate (Ornamental stone) Regulate the caliber of

Calibration (Ornamental stone) Operation of making the thickness of the statutory plates uniform

Calibrator (Ornamental stone) Machine with a rotating diamond coated head that performs the calibration

Capillarity (Plaster, Stucco; structural adhesives) Phenomenon associated with the liquid flow in capillaries due to surface tension

Cathode (Corrosion) Electrode where a reducing reaction takes place

Cathodic current (Corrosion) Current involved in a reduction reaction

Cathodic protection (Corrosion) Corrosion protection achieved by a decrease in the electrode potential (down to values close or even below the equilibrium potential of the metal's oxidation reaction). It can be achieved through the use of a generator (protection through impressed current) or by the use of a less noble metal (sacrificial anode)

Cation (Corrosion) Positively charged ion (e.g., H^+ or Fe^{2+})

Cathodic inhibitor (Corrosion) Inhibitor that interferes with the cathodic reaction. Typically, these are cations that migrate to cathode surfaces where they react, creating deposits and polarizing reactions taking place here

Cavitation (Corrosion) Formation of vapor bubbles in a liquid under the action of low localized pressures, followed by the instantaneous collapse of these bubbles, producing extremely high localized pressures

Cavitation—Corrosion (Corrosion) Form of corrosion caused by the joint action of corrosion and cavitation. Cavitation causes the removal of the corrosion products, increasing the exposure of the metal to the corrosive environment (see corrosion, cavitation)

Cement (Hydraulic binders; concrete) Hydraulic binder produced by heating from a mixture mainly of limestone and clay—forming clinker and subsequently finely grinded with gypsum ($CaSO_4{\cdot}2H_2O$) and, optionally, other additives. When mixed with water, the hydration reactions lead to the setting and hardening of the system with the ability to agglomerate other solid materials. The hardened material retains its strength and stability both underwater and when exposed to wet weather

Cementitious materials (Hydraulic binders) Designation that includes both pozzolanic materials and latent hydraulic binders, either naturally occurring or from industrial wastes. These additions take part in the hydration reactions altering the mechanical properties of the hardened cement-based materials

Ceramic tiles (wall and floor tiles) (Ceramic) thin plates made of clay and/or other inorganic raw materials, used as coatings for pavements and walls. Ceramic tiles are generally conformed by extrusion or pressing at room temperature (but may be shaped by other methods), followed by the drying and firing at temperatures high enough to obtain the required properties. Setts can be glazed (GL) or unglazed (UGL); they are refractory and are not affected by solar radiation (see *tile*)

Chamfer (Ornamental stone) Finished beveled or rounded edge

Characteristic strength (Concrete) Value of strength below which 5 % of the population of all possible strength determinations of the volume of concrete under consideration are expected to fall

Charges (Organic coatings) Inorganic substances in the form of particles, with low covering power, used in the formulation of organic coatings to increase its volume and modify their properties

Chemical tempering (Glass) Tempered produced by cation exchange between the lithium ions (Li^+) (located on the surface of the glass), and potassium (K^+) (outside environment), is performed by dipping the glass in a solution of potassium nitrate, for ~16 h at 400 °C. The exchange of potassium ions for lithium ions modifies the surface chemistry of the glass. The fact that potassium ions are larger than lithium ions makes glass surface under compression. The mechanical strength of the chemically tempered glass increases fivefold in relation to ordinary glass

Chemical modification (Wood) A treatment where a chemical reacts with components of wood (usually hydroxyl groups) resulting in a permanent chemical bond. An example of chemical modification of wood is acetylation

Clastic rock (Ornamental stone) Rock consisting of fragments from preexisting rocks which were produced by alteration and erosion and usually conveyed to a place of deposition

Cleaved or chipped slab (Ornamental stone) Facing slab with “coarse” appearance, divided into plates

Closed assembly time (Structural adhesives) Time elapsed between the time the substrates, with adhesive already applied, are brought into contact and the moment when heat and/or pressure is applied [NP 3672:1990]

Coated glass (Glass) Class of glasses (including anti-reflection, mirror, and low-emissive glasses) where a coating has been applied on a glass surface. It does not include enameling. Most common coatings are composed of metal or metallic oxide films. The coating process can be classified into two categories: *online*, when it takes place during the manufacturing process (usually inside the *float* chamber), and *offline*, when it occurs after the manufacturing process

Coatings (Polymer) Thin layer of material deposited over a surface with the purpose of protecting or decorating a substrate, in which case they are commonly referred to as paints. Polymeric coatings may or may not contain a volatile solvent, and the formation of the thin layer (film) may or may not involve a chemical reaction

Cohesion (Structural adhesives) Phenomenon by which the particles of a substance are held together by intermolecular forces [NP 3672:1990]

Cohesive failure (Plaster; Render) Rupture occurring within the mortar (its resistance being lower than that of the support), or rupture occurring at the support (when the mortar's resistance is higher than that of the support). In general, a disruption that occurs outside of the interface between the adhesive and the bonded surfaces

Column (Ornamental stone) Pillar based on appropriate base or executed directly on the floor having a variety of shapes, including rounded, segmented, and square, among others, serving to support vaults, entablatures, or as simple adornment

Common cements (Hydraulic binders) Cements whose composition, requirements, and conformity criteria are specified in the European standard EN 197-1:2000. This standard defines 27 distinct common cements including the composition of each product and the corresponding notation (that start with the letters "CEM"). These cements are grouped into five main cement types and described by their composition, main constituents, strength class, and rate of early strength development (see cement)

Compaction (Plaster; Render) Manual or mechanical process aimed at increasing the density of a fresh mortar

Compatibilizer (Polymers) Additive that lowers the interfacial tension in immiscible polymer blends and thereof enables control of their microstructure and morphology

Composite cements (Hydraulic binders) Hydraulic binders in which (1) the clinker is partially replaced with cementitious or mineral materials (in this case these additions are considered major constituents of cement) or (2) the cement is partially replaced by cementitious or mineral materials during the preparation of grout, mortar, or concrete (see cement)

Compressive strength (Ornamental stone) Physical and mechanical characteristic which assesses the ability of an element in rock (sample) to resist deformation when loaded in compression

Concentration cell (Corrosion) Galvanic cell formed by two identical electrodes, where the electromotive force is due to the difference in concentration of a common species in the two electrodes

Concrete (Concrete) Material formed by a mixture of cement, fine and coarse aggregates, and water, with or without the incorporation of admixtures, additions, or fibers, developing its properties by means of the cement hydration

Conformity assessment (Concrete) Systematic examination to determine whether the product satisfies the specified requirements

Consistency (Plaster; Render; Organic coatings) Viscosity of a non-Newtonian liquid at 1 s^{-1} shear rate

Contact adhesives (Polymer) Adhesives constituted by complex formulations including elastomers, fillers, adhesion promoters, etc.; they are currently used at room temperature by putting a layer of adhesive over one contact surface and pressing the second surface against the first one (see *adhesives*)

Coordination dimension (C) (Ceramic) Manufacturing dimension added to the joint width

Copolymer (Polymer) Polymers consisting of more than one type of monomer (see *monomer*, *polymer*)

Cork powder (Cork) Cork particles of particle size $\leq$0.25 mm (see cork)

Cork rubber or rubber cork (Cork) Agglomerate resulting from the agglomeration of cork granules with rubber

Cornice (Ornamental stone) Salient decoration on the upper part of a wall

Corrosion (Corrosion) Naturally occurring phenomenon commonly defined as the deterioration of a substance (usually a metal) or its properties because of a reaction with its environment

Corrosion current (Corrosion) Anodic current corresponding to the corrosion process of a metal at its open circuit potential. The value of this current is equal and of opposite signal to the cathode current; in this way, the total current flowing into or outside the system is zero

Corrosion fatigue (Corrosion) Fracture of a metal caused by the joint action of cyclic efforts and of an environment that can electrochemically or chemically attack it (see *corrosion*)

Corrosion in weldings (Corrosion) Localized corrosion of certain metals (particularly stainless steel austenitic) in areas near the weld beads (see *corrosion*, *intergranular corrosion*)

Corrosion inhibitor (Corrosion) Substance which, when added in small concentrations to the corrosive environment, decreases the corrosion rate

Corrosion of polymers (Corrosion) Although not corroding as metals do, polymers also suffer deterioration by actions of the environment, suffering from swelling, loss of mechanical properties, softening, hardening, discoloration, etc., that fall within the definition of corrosion (see corrosion)

Corrosion potential (Corrosion) Electrode potential of a metal in a given environment, under conditions of open circuit (no external flux of current). Under these conditions, the anodic (corrosion) and cathodic reactions occur at the same rate, i.e., the electrons produced in the oxidation are consumed in the reduction (see corrosion)

Corrosion rate (Corrosion) Speed at which a metal deteriorates in a specific environment, being related to the intensity of the corrosion process. It may be presented as loss in mass per unit area and unit of time or, in the case of uniform corrosion, as loss of thickness per time unit. Using Faraday's equation, it can relate to the corrosion current density, determined by electrochemical methods

Corrosion of stone materials (Corrosion) Similarly to what happens in other systems (see corrosion of polymers), this process is not limited to one electrochemical phenomenon and is often defined as "stone decay." However, since it is a phenomenon of degradation by the environment, it is within the definition of corrosion (see corrosion)

Corrosivity (Corrosion) Aggressiveness of an environment for a given material

Cover thickness (Corrosion) Thickness of concrete cover applied over the reinforcing steel

Creep (Concrete; Polymer) Increased deformation over time of a material subject to a constant load

Crosscut (Ornamental stone) Parallel cut to natural strata level

Cross-linked elastomers (Polymer) Elastomers formed by a network of polymer chains bound to one another at selected points (cross-links). Cross-linking may be promoted by chemical reactions (chemical cross-links) or by physical interactions (physical cross-links) (see *elastomers*)

Cross-linking (process) (Polymer) Formation of a polymer chain network by promoting chemical reactions between reactive groups belonging to different chains (chemical cross-linking) or by physical interactions (physical cross-linking). Chemical cross-linking includes vulcanization (cross-linking with sulfur), the use of polyfunctional molecules or monomers (cross-linking agents), or others. Physical cross-linking is reversible and may be promoted by fillers or a consequence of chain segregation in block copolymers. The amount of cross-linking must be high enough to get a solid material but much smaller than the one required for thermosets (see monomer, polymer, polymerization)

Crevice corrosion (Corrosion) Localized form of corrosion, very common and dangerous, that occurs in occluded areas of passive metals, being associated to the existence of zones with stagnant solution, which renovation and aeration are difficult. A differential aeration cell is formed with the oxidation reaction being located in the less aerated crevice, where the oxygen content is lower

Crown glass (Glass) Glass produced by a manual method where a piece of glass is supported in a blow tube and quickly rotated to create disk or crown-glass pieces in disk or crown-shaped forms

Cure (Structural adhesives) Process of development of an adhesive strength properties trough a chemical reaction [NP 3672:1990]

Curing (Concrete) Set of procedures used to prevent the evaporation of water from the concrete surface

Curing (Polymers; Polymer matrix composites) Term generally used to designate the cross-linking chemistry of thermosets. In cross-linking of thermosets almost all of the reactive chemical groups preexisting in the resin are involved resulting in a polymer network

Cork sheet (Cork) Product resulting from the lamination of cork blocks

Crafted slab (Ornamental stone) Slab with modified appearance as a result of one or more treatments (e.g., thermal or mechanical) of its surface

Cutback Bitumen (Binders and Bituminous materials) Bitumen whose viscosity was reduced by adding a relatively volatile fluxing (CEN)

Cutter (Ornamental stone) Machine used for continuous cutting (milling); side cutting tool, which is operated by a vertical or horizontal milling machine

Curing time, Setting time (Structural adhesives) Period of time necessary for an adhesive in an assembly to cure or set under specified conditions of temperature or pressure, or both [NP 3672:1990]

D

Decorated glass (Glass) Class of glasses (including silkscreen printed and rolled plate glasses) that enables light transmission to be controlled, reduces solar energy gain, and can create distinct environments, with or without visibility, defining levels of privacy

Defect (Wood) Physical, morphological, or anatomical singularity of wood that may limit its use

Deformability (Render; Plaster) Ability of a hardened mortar to be deformed under the action of stresses without destruction of the structure

Degradation (Polymer) Deterioration of a material with loss of performance; the development of the "degree of loss" may be monitored by successive measurements of one or more selected properties (mechanical, electrical, optical, etc.). The mechanisms involved are multiple: hydrolysis, thermal degradation, rust, UV radiation, solvents, depolymerization of others

Degree of crystallinity (Polymer) Volume fraction of crystallized material presented in a given volume of a polymer. In some civil engineering applications, the degree of crystallinity is considered as the mass fraction of crystallized polymer

Degree of polymerization (Polymer) Number of monomers per polymer chain (see monomer, polymer)

Density (Ornamental stone) Mass that exists in certain unit of volume or surface with length

Desboia (Cork) First extraction in the young cork trees

Diaclase (Ornamental stone) Natural crack in a rocky block, without having occurred displacement throughout the crack

Diamond abrasive (Ornamental stone) Generic designation of hard and wear-resistant substances used to wear and polish, in which the main component is diamond

Diamond blades for sawing (Ornamental stone) Steel blades in which (welded or brazed) diamond inserts or segments are integrated

Diamond disk (Ornamental stone) Tool whose circular contact surface with the stone is diamond (continuous or segmented)

Diamond drill (Ornamental stone) Tool whose circular contact surface with the stone is achieved using diamond grit (continuous or segmented)

Differential aeration (Corrosion) Difference in dissolved oxygen concentration at two points of the same system

Differential aeration cell (Corrosion) Concentration cell caused by a gradient of oxygen concentrations between the two electrodes (see concentration cell)

Diluent (Organic coatings) Volatile liquid, partially or completely miscible with its vehicle, which, added to a paint or varnish during the manufacturing process or at the time of application, reduces its viscosity

Dispersion (Organic coatings) Intimate mixture of a liquid with a solid placed in it in the form of finely divided particles

Dome (Ornamental stone) Construction raised in arch; arched ceiling

Double glazing (Glass) Structure consisting of two (or more) sheets of glass separated by a spacer bar that hermetically seals the cavity width (usually filled with dehydrated air) between the two glasses. In addition to the seal, the presence of a desiccant agent is recommended for moisture absorption inside the glass and to ensure long-term performance. The type of frame is crucial in the performance of the double glass

Draining bituminous concrete (Binders and Bituminous materials) Bituminous mixture of discontinuous grain size, formulated so as to obtain a significant proportion of empty interconnectors (20 % volume or more) to facilitate the passage of water (CEN) (see *concrete*)

Dry cutting (Ornamental stone) Cutting process without the use of coolant

Dry pressed tiles (type B) (Ceramic) Tiles formed from a powder mix finely milled, conformed in high-pressure molds (see *ceramic tiles*)

Dry strength (Structural adhesives) Strength of an adhesive joint determined immediately after drying under specified conditions [NP 3672:1990].

Drying (Structural adhesives) Set of physical and/or chemical transformations that cause an adhesive to pass from the liquid or pasty state to the solid state [NP 3672:1990]

Drying oil (Organic coatings) Liquid animal or vegetable oils that react with oxygen to form solid films

Ductile fracture (Glass) Type of fracture in which significant deformation (plastic deformation) of the test specimen occurs before rupture. In ductile fracture, the forming energy of a critical crack is much smaller than the crack's propagation energy

Durability (Plaster; Render; Concrete) Capacity of a building, system, component, structure, or product to maintain a minimum performance for a given time (lifetime) under the action of different chemical, mechanical, and climatic conditions

Dynamic fatigue (Polymer) Test whereby the resistance of a test specimen to a cyclic charge is measured

E

Earlywood (Wood) Part of the growth layer formed in the initial phase of a tree's growth period. It is usually less dense and less dark than the xylem of latewood

Edge (Ornamental stone) Line determined by the intersection of the planes of the faces of an element in stone. The edges may undergo different types of finishing in the final stage of preparation of the product

Effective water content (Concrete) Difference between the total amount of water present in the fresh concrete and the amount of water absorbed by the aggregates

Efflorescence (Plaster; Stucco) Formation of salt crystals on the surface of a mortar

Elastic recovery (Polymer) Test whereby the response (deformation) after interruption of a fluency test is measured (response to a rectangular voltage wave)

Elastomer (Polymer; Structural adhesives) Designation that encompasses polymers with a mechanical behavior similar to that of natural vulcanized rubber at room temperature: they can endure high deformation (over 100 %) without snapping and quickly recover their initial shape and dimensions after cessation of application of the load

Electrochemical series (Corrosion) List of chemical elements, ordered according to the value of their standard electrochemical (reduction) potentials

Electromotive force (Corrosion) Potential difference of a galvanic cell when the current flowing through the system is null

Embedding (Ornamental stone) Carving; damascening; introducing pieces of a different color or texture in furniture, floors, etc.

Embossing (Ornamental stone) Carving with chisel; to mark with stamp

Emulsion (Organic coatings) Intimate mixture of two nonmiscible liquids, one of them (the emulsionized) being dispersed in the other (the dispersing liquid) in the form of droplets

Enamel (Organic coatings) Finish that generates a film with a more or less shiny appearance and characterized by a good lacquering

Engobed tiles (Ceramic) Tiles to which a surface coating based on clay is applied with a matte finish that can be permeable or impermeable. These are classified as glazed (UGL) (see *ceramic tiles*)

Environmental actions (Concrete) Those chemical and physical actions to which the concrete is exposed and which result in effects on the concrete or reinforcement or embedded metal that are not considered as loads in structural design

Environmentally induced cracking (Corrosion) Corrosion involving a synergistic effect between the corrosive environment and the applied mechanical stress (see corrosion)

E-pH diagram (Corrosion) The same as the Pourbaix diagram

Equilibrium moisture content (Wood) Stabilized moisture content corresponding to the environmental conditions of the site of application

Erosion-Corrosion (Corrosion) Increase of the rate of attack on a metal due to relative motion between a corrosive fluid and the metal surface (see corrosion)

Extruded tiles (type A) (Ceramic) Tiles whose pulp is conformed in the plastic state at an extruder, with the bar being cut into tiles with predetermined dimensions (see *ceramic tiles*)

Extrusive rock (Ornamental stone) Igneous rock brought to the surface of the earth in a cast product condition

F

Façade (Ornamental stone) Vertical envelope of a building

Face (Ornamental stone) Surface of an exposed piece of stone

Falca (Cork) Virgin cork, usually from pruning and mechanically or manually extracted (ax, adze), lengthwise according to the branch, presenting adherent fragments of inner bark and xylem

False joint (Ornamental stones) Finishing process where nonexistent joint is reproduced (see joint)

Fatty oil (Organic coatings) Name given to vegetal or animal oils whose basic components are triglycerides of fatty acids

Feedstock (Ornamental stone) Material which can give rise to one or more types of products

Fiber (Wood) Long and narrow cell (or group of cells) constituting a large part of the xylem (mainly arranged parallel to the axis of the trunk or branches)

Fiber (Polymer matrix composites) Material with a geometry in which the length/diameter ratio is >100 and is used as a reinforcing element

Fiberglass (Plaster; Render) Inorganic and amorphous fiber generally from silica, or modified silica, obtained by different methods ("spray," drawing of glass test specimen, etc.) and usually used for reinforcement, either in fabric or mesh form

Filiform corrosion (Corrosion) Occurs very often in coated or painted surfaces and consists in the development of very fine filaments between the metal and the coating, which propagate along the surface, causing delamination of the coating (see corrosion)

Filler (Structural adhesives) Relatively inert solid substance, generally inorganic, added to an adhesive to improve its working properties, permanence, strength, or other qualities (EN 923:2005 + A1:2008)

Filler (Organic coatings) Inorganic substance in the form of particles with weak coverage power that, incorporated into a matrix (paint, among others), alters its characteristics

Filler (Hydraulic binders; Binders and Bituminous materials) Addition of finely grinded and chemically inert, which modify the mechanical properties of the materials in which they are incorporated (cement, bituminous materials, etc.) by filling the pores

Fillers (Polymer) Substances added in order to occupy the free volume of the piece with lower cost materials (calcium carbonate, silica, kaolin, etc.)

Filler (or stuffing) (Polymer matrix composites) Material that is usually inorganic and relatively cost-reduced, added to the polymer resin, which tends to reduce the final cost of the product and to improve performance relative to some properties

Filonian rocks (Ornamental stone) Igneous rock that crystallized under intermediate conditions between plutonic and volcanic rocks

Filter press (Ornamental stone) Equipment that forms part of the water purification system and separates the water from the sludge

Fining (Glass) Stage during which chemically and/or physically dissolved gases in the vitreous molten glass are eliminated (inside the melting furnace)

Finishing (Organic coatings) Top layer in a painting scheme

Finishing (Ornamental stone) Final work normally made on a stone product surface

Finishing with sand blasting (Ornamental stone) Superficial finishing in which an abrasive mixture with sand is used and sprayed with pressure (see *finishing*)

Fire-retarding glass (Glass) Safety glass that prevents the passage of smoke, flame, and heat (class of Safety Glass)

Flank (Ornamental stone) Surfaces of a slab, perpendicular to the larger faces (see face)

Flaw (Ornamental stone) Fractured rock mass with vertical and horizontal movement

Flexible pavement (Binders and Bituminous materials) Pavement with asphalt and concrete top layer, supported on a base layer of non-treated granular materials, or treated with bituminous binders

Flexural strength (Plaster; Render) Tensile strength of a mortar, determined by the application of a three-point bending force

Flexural strength (Ornamental stone) Physical and mechanical characteristic which assesses the ability of an element in rock (sample) to resist deformation in the direction perpendicular to the actuating force

Float (Glass) Current process of flat glass forming. The vitreous molten (~1,150 °C) is poured into the *float* chamber over a molten metallic tin (Sn^0) bath. The atmosphere in the interior of the float chamber is extremely reductive (N_2 with 0.5 % H_2). Glass and molten tin are immiscible, exhibiting a flat contact surface. Over the molten tin, a flat polished sheet of glass is formed, which, as progress in the float chamber is made, cools and solidifies (patent-pending by Pilkington Brothers, UK)

Folded chamfer (Ornamental stone) Continuous slot made on one side of a plate to allow the introduction of anchoring systems (see anchor)

Fossil (Ornamental stone) Biological samples (animal or plant) from past ages that have been preserved by integration into rocks of contemporary forming

Fracture (Ornamental stone) Defect or crack in a stone. Growth and propagation process of a crack to the surface of the piece, causing its fragmentation into two or more pieces

Fresh concrete (Concrete) Completely mixed concrete still in a condition of being workable (see concrete)

Fretting corrosion (Corrosion) Acceleration of corrosion by the joint action of a corrosive medium and the movements of slipping or vibration that occur in the contact areas between materials (see *corrosion*)

Frost resistance (Ornamental stone) Number of cycles in which stone resists to frost, whereas the main causes of failure are loss of bending resistance >20 %, volume loss in more than 1 %, or the decrease in resonance frequency of 30 % or more. To this end, cycles of exposure of ice to ice must be undertaken (typically: −12.5 °C) and thaw in water (typically: +20 °C)

Functionality of the cross-linking point (Polymer) Number of substrings connected to a cross-linking point (network node of polymer network with minimum value 3)

Fiber saturation point or FSP (Wood) Moisture content of wood when its cell walls are saturated with water without evidence of the presence of water in its cellular cavities (lumens). Moisture content corresponding to the fiber saturation point, for forest species of temperate climates being about 28–30 %

Fissure (Wood) Separation of wood fibers in the longitudinal direction

G

Galvanic corrosion (Corrosion) Electrochemical corrosion of a metal due to electrical contact with a more noble metal in a corrosive environment. The less noble metal oxidizes, while the more noble metal acts as the cathode (see corrosion)

Galvanic series (Corrosion) List of metals and alloys arranged according to the increasing value of its corrosion potential in a particular environment. A metal that is higher in the galvanic series is nobler and behaves as a cathode when in contact with those who are below, less noble and, therefore, tend to corrode

Galvanizing (Corrosion) Zinc coating, typically applied on steel by immersion in a bath of molten zinc or electrolytic deposition (electrogalvanizing)

Gasket (Cork) parts whose shape and thickness are suitable as connecting elements intended to dampen vibration, compensate for dimensional variations of adjacent parts, and/or to ensure the watertightness of the connection

General purpose mortar (Plaster; Render) Mortar that meets the general requirements without having special features (see mortar)

Glass (Glass) Noncrystalline (or amorphous) material traditionally obtained by rapid cooling of a melt and characterized by glass transition temperature

Glass transition temperature, T_g (Structural adhesives) Temperature to which an adhesive or an assembly is subjected to cure the adhesive [ASTM D 907-04]

Glass transition temperature, T_g (Glass; Structural adhesives; Polymer) Temperature characteristic of an amorphous material (glass, polymer), below which it is no longer in thermodynamic equilibrium; as a result, during cooling, a sharp increase in viscosity (glass) or elastic moduli (polymer) in the value of several orders of magnitude can be observed (103, 104, or more). In addition to the structure and chemical composition, T_g depends on the cooling rate and the thermal history of the sample

Glazed tiles (Ceramic) Tiles that receive a surface vitreous coating that is waterproof. These are classified as glazed (UGL) (see *ceramic tiles*)

Gloss (Organic coatings) Capacity of a film to reflect or diffuse the light

Glued laminated timber (Wood) Structural product obtained by gluing wood lamellas, usually 30 to 45 mm thick each, with the wood fibers oriented parallel to each other

Gneiss (Ornamental stone) Regional slime metamorphic rock, shale, gray-colored granite-like with dark-colored granular texture

Graft copolymer (Polymer) Copolymer constituted by a main chain of a given polymer, in which substrings constituted by other monomers are grafted (see *copolymer*)

Grain/Texture (Wood) Visual appearance of the wood, depending on its anatomical structure and the width and regularity of growth layers

Grain direction (Wood) Direction of the general arrangement of wood fibers

Grain size (Ornamental stone) Average size of the grains or crystals in a rock

Granulate (Cork) Cork fragments of various sizes, from grinding, crushing, or milling, followed by summary sieving

Granules (Cork) Fragments obtained by grinding, milling, or crushing of raw cork, prepared cork, or cork transformed by carving and/or its waste materials with a particle size from 0.25 to 45 mm

Gravel pit (Binders and Bituminous materials) Place from which to draw aggregates with alluvial origin

Green wood (Wood) Wood which has not yet undergone the drying process until or below the fibers' saturation point

Grinding machine (Ornamental stone) Machine that prepares plates and introduces a primary polishing before initiating the polishing operation

Grit (Ornamental stone) Small fragments in the form of granules or vanes to which the weld metal (steel or iron) is reduced. Grit can also be formed by corundum (mineral based on aluminum oxide, which represents a value of 9 in the Mohs hardness scale)

Grout (Structural adhesives) Aqueous mixture of materials such as cement and bentonite, clay, and chemicals, among others that form a suspension, an emulsion, or a solution

Growth layer (Wood) Layer of wood produced during one growing season. The width of the growth layer depends on the species and growth conditions. In species of the temperate zones each layer reflects a full year's growth and is called annual growth ring

Growth rate (Wood) Growth expressed by the average width of the annual growth rings

H

Handrail (Ornamental stone) Piece that runs along a staircase with a supporting function bar that serves as a backboard or a parapet in any balcony

Hardened concrete (Concrete) Concrete in the solid state that has developed some mechanical resistance (see *concrete*)

Hardener (Structural adhesives) Substance that initiates and/or regulates the cross-linking reactions in adhesives [NP 3672:1990]

Hardening (Concrete) Phenomena following setting of cement paste where the mixture (paste, mortar, or concrete) is in a solid state and is developing a certain strength

Hardness (Plaster; Render; Ornamental stone; Polymer) Characteristic property of a solid material, which expresses the surface resistance to permanent deformation (penetration, risk) usually caused by a puncture

Hardwood (Wood) Wood from broad-leaved trees

Head (Ornamental stone) Mechanical drive of many machines that holds the tool

Heartwood (Wood) Part of the xylem/wood of the standing tree that does not contain living cells or no longer conducts crude sap. The heartwood is usually darker than the sapwood, but is not always clearly differentiable from this

Heavy aggregate (Concrete) Aggregate with $\geq$3,000 kg/m^3 density after drying in oven (see *aggregate*)

Heavy concrete (Concrete) Concrete with a dry density of $>$2,600 kg/m^3 (see *concrete*)

Hiding the (Organic coatings) Capacity of a coating to cover the color or color differences in the substrate underneath

High strength concrete (Concrete) Concrete with a compressive strength class higher than C50/60, in the case of normal concrete or heavy-weight concrete, and higher than LC50/55, in the case of lightweight concrete (see concrete)

Homogenizing (Glass) Process that occurs inside the glass melting furnace and aims to obtain a melt of uniform composition without any temperature gradient

Homopolymer (Polymer) Polymer obtained by polymerizing a single type of chemical monomer

Hot applied adhesives (Polymer) Polymer mainly composed of thermoplastic adhesives, applied in the form of melt and whose adhesion occurs after cooling (see adhesives)

Hydration of cement (Concrete) Series of reactions that occur with the cement when in contact with water causing the mixture to harden, even underwater (see cement)

Hydraulic binders (Hydraulic binders) Substances that chemically react with water converting the water-binder system with plastic consistency into a solid matrix with the ability to agglomerate other solid materials. This hardening process occurs spontaneously at room temperature. The hardened materials are stable, both underwater and exposed to wet weather

Hydraulic lime (Hydraulic binders) Construction material obtained through thermal activation of limestone with significant clay content (between 6.5 and 20 % by mass) in its constitution. The clay provides the hydraulicity and the plastic properties to the lime

Hydrogen embrittlement (Corrosion) Loss of a material's ductility due to the presence of hydrogen (atomic or molecular). Hydrogen can also penetrate the metal from hydrogen-rich atmospheres, for instance, during thermal treatment or weldings, and its presence in the crystal lattice will lead to a degradation of the mechanical and metallurgical properties of the metal

Hydrophilic film (Glass) Film (or coating) of hydrophilic nature, i.e., with affinity towards the water molecule (from the Greek hydros (water) and philia (affinity towards)). A hydrophilic film deposited on a glass alters the contact angle of a drop of water (from 30–40° to 4–7°), thereby forming a continuous thin film of water on the glass, easier to remove

I

Igneous rock (Ornamental stone) Rock formed by the solidification of molten material (magma)

Immiscible polymer mixtures (Polymer) Mixtures in which it is thermodynamically impossible to form a single stable phase, thus occurring separation in phases corresponding to each one of its components. That trend can be hindered (but not eliminated) through appropriate formulation (use of "compatibilizers") (see polymer)

Immunity (Corrosion) State of a metal that is under the conditions that correspond to its thermodynamic stability, so that corrosion is not thermodynamically possible. It occurs when the metal's potential is lower than the equilibrium potential of its oxidation reaction

Impact resistance (Polymer) It is a measure of the energy per unit crack surface, needed to break a specimen by impact, i.e., by application of a given load in a very short time lapse. Its determination involves the measurement of the rupture energy per unit crack surface of a representative sample extracted from a statistical population of specimens of the same material. The impact resistance is estimated from the required energy per unit crack surface, needed to break 50 % of the elements of the representative sample. Since the critical growth of a crack involves a complex sequence of processes, impact resistance estimations improve as the test conditions become closer to real situations of impact

Impermeability (Plasters; Render) Ability of mortar to prevent water penetration under a given pressure

Impregnability (Wood) Impregnation capability of wood by liquids, for example, a preservative

Impressed current (Corrosion) Current supplied by an external generator in a cathodic protection system

Inorganic polymers (Polymer) Polymer whose main chain does not have carbon atoms (see polymer)

Insect (Cork) Defect caused by larvae or insects that create galleries inside the cork, making it usable only for granulates and/or agglomerates

Intergranular corrosion (Corrosion) Localized corrosion in the grain boundaries (see corrosion)

Interstitial electrolyte (Corrosion) Liquid phase existing in concrete pores

Intrusive rock (Ornamental stone) Igneous rock which crystallizes in pockets of deeper levels or between layers of other rocks

J

Joint (Ornamental stone) Connection, line, or surface where two or more objects adhere; insert aimed at connecting two pieces or objects

K

Knot (Wood) Portion of a branch contained in the piece of timber

L

Lacquer (Polymer) Coatings consisting of polymer suspensions in which the film formation results from evaporation of the suspension medium alone

Laminate (Polymer matrix composites) Composite material consisting of several sheets or layers

Laminated glass (Glass) Glass consisting of two (or more) sheets of glass held together by one (or more) of synthetic film of polyvinyl butyral (PVB). After the placement of the film between the glass sheets, the adhesion is promoted in autoclave by thermal treatment under pressure. Once sealed, this composite material (a glass and PVB sandwich) behaves like a cohesive unit and has the appearance of a single glass. If fractured, it retains vitreous fragments with sharp edges, preventing its fall, potential cause for accident, while continuing to act as a barrier to the entry of people or objects (class of safety glass)

Latent hydraulic binders (Hydraulic binders) Compounds consisting of calcium silicates and aluminates which harden spontaneously by reacting with water. However, the hardening process only becomes significant in the presence of an alkaline activator

Lathe (Ornamental stone) Cutting and sawing machine in which a frame is integrated, made of several metal blades used for cutting stone blocks by abrasion, caused by the blades' traversing movement, which can be diamonded in the case of marbles and steel only in igneous rocks (granite)

Lenticels or pores (Cork) Cylindrical or conical profile channels with irregular section, with walls sometimes filled with powdery cortical cells that cross the suberous tissue, from the belly to the outer layer, and that allow gas exchange between the atmosphere and the various cell layers

Life cycle (Plaster; Render; Concrete, Bituminous binders and materials; Ornamental stone; Env. Imp. and LCA) Period of time during which the performance of a product remains at a level that is compatible with the function for which it was designed, ending due to malfunction or obsolescence

Light concrete (Concrete) Concrete with a dry density between 800 and 2,000 kg/m^3. It is produced partially or completely using lightweight aggregate (see *concrete*)

Lightweight aggregate (Render; Plaster; Concrete) Aggregates with density <800 kg/m^3 [concrete] whose aggregate density, after drying in is $\leq 2{,}000$ kg/m^3, and bulk density is $\leq 1{,}200$ kg/m^3 (see *aggregate*)

Lime (Hydraulic binders) common name of calcium oxide (CaO). To be used for construction purposes it is obtained through thermal activation of limestone and may include all forms of calcium and magnesium oxides or hydroxides (CaO, MgO, $Ca(OH)_2$, $Mg(OH)_2$)

Limestone (Ornamental stone) Sedimentary rock comprised essentially by carbonates. The two most important are calcite and dolomite

Longitudinal shear strength (Structural adhesives) Force per unit area necessary to bring an adhesive joint to the point of failure, under specified conditions by means of a force applied parallel to the joint (i.e., in a shear mode) [NP3672:1990]

Latewood (Wood) Part of the growth layer formed in the final phase of a tree's growth period. It is usually denser and darker than the xylem of earlywood

Low-emissivity glass (Glass) Glass where one of the surfaces is coated with an invisible metallic film that reflects UV radiation (class of Coated Glasses)

Layer (Organic coatings) Continuous deposit of a paint or equivalent, achieved in one application stage only

M

Manual molding (hand layup or wet layup) (Polymer matrix composites) Manufacturing process in which the reinforcing layers pre-impregnated or subsequently impregnated by the matrix are placed manually into a mold and subsequently cured with the desired shape

Manufacturing dimension (W) (Ceramic) Specified length, width, and thickness of a tile which must be consistent within allowable tolerances

Marble (Ornamental stone) Metamorphosed limestone of granular sugar-type texture formed by the recrystallization of a carbonate rock. Commercially, the group of marbles includes rocks that are prone to develop polishing, such as limestone, crystalline, and microcrystalline

Marbling (Cork) Cork area infested by a bluish fungus, sometimes frequent, providing a visual change which is disadvantageous for some applications (see cork)

Mat (mats and fabrics) (Polymer matrix composites) Reinforcement geometry embodied in a flat form in which fibers may be disposed in various directions through a large array of products with short or continuous fibers arranged randomly (chopped strand mat or continuous strand mat, respectively), biaxially (typically 0°/90° or 45°/−45°) or triaxially (typically 0°/45°/−45°) oriented continuous fibers, which may or may not be interlaced (woven fabrics or nonwoven fabrics, respectively)

Matrix (Polymer matrix composites) Material, usually polymeric in nature, that embeds the reinforcing fibers

Melting (Glass) Raw materials (weighted, mixed, and pre-heated), after being introduced into the melting furnace, suffer heating, dehydration, decomposition, and solid state chemical reactions, yielding a viscous and glassy molten material

MEMS (Nanomaterials) According to the Anglo-Saxon nomenclature, it refers to Micro-Electro-Mechanical Systems

Metamorphic rock (Ornamental stone) Includes all the rocks that were formed from parent or preexisting rock by a type of metamorphism

Mill column (Ornamental) Vertical cutting machine (with pedestal and countertop)

Milling machine (Ornamental stone) Machine for manufacturing special shapes, computer controlled; pantograph

Mimic (Nanomaterials) In nanotechnology, it means to copy a natural (biological or mineral) nanostructure

Mineral plastering mortar (Plaster; Render) Mixture of one or more inorganic binders, aggregates, with eventual additions and/or admixtures, used for indoor plastering or outside (see mortar)

Mirror glass (Glass) Float glass with a surface coating which gives it specific optical and thermal performances. Mirror glass allows the maximization of the reflection component of light and minimization of the transmission component (class of Coated Glasses)

Miscible polymer mixtures (Polymer) Thermodynamic equilibrium mixtures constituting a single phase (see polymer)

Mixed inhibitor (Corrosion) Inhibitor which acts both on the anodic and cathodic areas of the metal

Modified Bitumen (Binders and bituminous materials) Bitumen whose rheological properties were modified during the manufacturing process through the use of a chemical agent such as natural rubber, synthetic polymer, sulfur, and certain organometallic compounds. Modified bitumens can be used directly or in the fluidized or emulsified form or even, for example, with natural asphalt

Modular dimension (M) (Ceramic) Tiles and dimension-based modules M, 2 M, 3 M, and 5 M and also in their multiples or subdivisions, except tiles with surface area $<$9,000 mm^2. *Note*: M = 100 mm

Modulus of elasticity or Young's modulus (Concrete) The load that is necessary to apply on concrete, under a pure elastic regime, to obtain a unit elongation

Moisture content (Wood) Mass of water in wood, expressed as weight percentage relative to the oven dry mass of that wood

Monolayer coating (Plaster; Render) Mortar designed for coating, applied in a single layer, which fulfills all the protective and decorative functions achieved by a multilayer system

Monomer (Polymer) It can be used in various purposes: (1) "chemical monomer," that is, the smaller chemical unit that is repeated throughout the polymeric chain; (2) in chemical engineering jargon, "monomer" designates the feedstock introduced into the polymerization reactor, even consisting of oligomers and does not coincide with the "chemical monomer"; and (3) in the physical modeling of polymer chains, it denotes the Kuhn segment or thermodynamic segment (physical monomer)

Mortar (Structural adhesives) Product able to maintain in a state of adhesion two surfaces of one or more materials which are far apart from one another. Due to the high volume that mortar must make up, it must have special characteristics: it should be a penetrating material in order to fill inaccessible areas; it should be able to eliminate the air trapped during curing, and be sufficiently stable to avoid the separation of the components under gravity (i.e., segregation)

Mortar (Plaster; Render) Mixture of one or more organic or inorganic binders, aggregates, fillers, additions, and/or admixtures

Mortar made on site or traditional mortar (Plasters; Render) Mortar comprising primary constituents (e.g., binders, aggregates, and water) dosed and mixed on site (see *mortar*)

Mosaic (Ornamental stone) Tile

Mounting holes (Ornamental stone) Openings that allow the realization of a fixing operation through bolting or clamping systems

Mud (or sludge) (Ornamental stone) Concentrated slurry produced by the processes of sawing, cutting, and polishing. Usually, mud is the product originating from carbonate rocks and sludge from siliceous rocks

Multiblade (Ornamental stone) Cutting machine that uses a variable number of diamonded disks

Multidisk cutter (Ornamental stone) Bridge sawing machine using multiple disks simultaneously

N

Nano (Nanomaterials) (Symbol n) is a prefix meaning one billionth. It was first used in the metric system, for example, a nanometer (nm) is one billionth of a meter, i.e., 10^{-9} m, and equals the length of 10 hydrogen atoms or 5 silicon atoms aligned. Nano originates from the Greek word for dwarf (νάνος)

Nanomaterial (Nanomaterials) Artificial nanomaterial (or nanostructure) with at least one critical dimension (height, length, depth) below 100 nm. Nanomaterials may be classified into 0D (nanoparticles), 1D (nanotubes, nanofibers, and nanofilaments), 2D (nanofilms and nanocoatings), and 3D (bulk), which represent the number of dimensions not confined to nanoscale

Nanotechnology (Nanomaterials) Focuses on the study and development of new functional artificial materials/systems whose structures and components exhibited novel and significantly improved physical, chemical, and biological properties, due to their nanoscale size

Natural durability (Wood) Intrinsic resistance to attack by wood destroying organisms (fungi, insects, and marine wood borer)

Neutral rock (Ornamental stone) Igneous rock containing more than 52 wt% and less than 66 wt% silica

Noble metal (Corrosion) Metal that is resistant to corrosion and oxidation in moist air and that can be found in nature under its metallic (unoxidized) form

Nominal size (Ceramic) Dimension used to designate the product

Nominal size (Ornamental stone) Any specific measurements for the manufacture of a slab, for which the actual dimensions should be set within the tolerances allowed

Nonreactive coatings (Polymer) Produced from hot applying polymeric waxes, so as to obtain a convenient viscosity

O

Obsidian (Glass) Natural glass, usually of volcanic origin, which by its relative abundance has supposedly been the more commonly used in artifacts throughout prehistory

Onyx (Ornamental stone) Zoned mineral, with dullness, which is considered a variety of fine agate

Opacity (Organic coatings) Ability of a paint to cover, after drying, color or differences in color in the applied basis; also called Hiding power.

Open circuit potential (Corrosion) The same as (see corrosion potential)

Open time, open assembly time (Structural adhesives) Maximum time interval between adhesive application to the adherents and assembly of the adhesive joint for the adhesion to be effective [NP 3672:1990]

Ordinary glass (Glass) (Float) Flat glass just annealed (the simplest manufactured flat glass)

Ovendry wood (Wood) Wood with a moisture content of 0 %. The anhydrous state of wood is achieved through its drying in a ventilated oven at a temperature (103 ± 2 °C) until a constant mass is achieved

Oxidation (Corrosion) Electrochemical reaction in which a species loses electrons

P

Paint system (Organic coatings) Set of paints, lacquers, or similar products that, when applied sequentially in a convenient order, correspond to the coating

Parquet (Cork) Agglomerated cork tiles of various sizes for floor coatings, with a density usually greater than 400 kg/m^3 (see cork)

Passivation (Corrosion) Very significant decrease in the corrosion rate of a metal due to the formation of a protective film of corrosion products (oxides/hydroxides) (see *corrosion*)

Passivation potential (Corrosion) Minimum value of the potential that allows passivation of a given metal in a particular environment (see corrosion)

Passive metal (Corrosion) Metal that, once oxidized, forms a protective film of oxides/hydroxides. Although being in thermodynamic conditions corresponding to its oxidation, the corrosion rate of the metal is very slow (passive corrosion) due to the shielding effect of the protective film

Pavement (Binders and bituminous materials) Part of the road specially prepared for vehicle traffic

Peel strength (Structural adhesives) Force per unit width applied at an angle between 90 and 180° relative to the adhesive joint needed to bring an adhesive joint to the point of failure or to maintain a specific rate of failure [NP 3672:1990]

Permeability (Organic coatings) Capacity of a dry film to let substances such as oxygen, water, and ions to diffuse across it

Photocatalytic film (Glass) Film (or coating), generally consisting of titania deposited on one surface of the float glass. This film is photo-activated by UV radiation; the oxygen species produced in the photocatalytic reactions crack, in a gradual yet continuous manner, chemical bonds of the organic compounds deposited on the glass

Piece (Cork) Piece of cork of small dimensions (<400 cm^2)

Pith (Wood) Central core of the tree trunk surrounded by the first growth layers, formed mainly by parenchymal tissue

Pitting corrosion (Corrosion) Localized form of corrosion that causes holes with a small area and that can reach a considerable depth. It is usually associated with passive metals in environments containing aggressive ions such as halides (see corrosion)

Plank (Cork) Prepared cork of a quality susceptible to further transformation through hoist

Plaster and lime mortar (Plaster; Render) Mortar containing at least 50 %wt calcium sulfate as a main binder and more than 5 % lime (calcium hydroxide) (see mortar)

Plaster mortar (Plaster; Render) Mortar containing at least 50 wt% of calcium sulfate as a main binder and no more than 5 wt% of lime (calcium hydroxide) (see mortar)

Plaster system (multilayer) (Plaster; Render) Sequence of mortar layers applied on a substrate, possibly reinforced and/or pre-treated

Plastic viscosity (Concrete) Angular coefficient of the curve representing the shear stress versus shear strain rate above the yield stress value

Plasticizer (Plaster; Render; Concrete) Admixture that allows a reduction of the amount of mixing water without affecting the consistency, or allowing an increase in fluidity, without affecting the amount of mixing water, or both effects simultaneously

Plate (Cork) Rigid or semirigid piece generally rectangular-shaped whose thickness is significantly smaller than other dimensions

Plate (Ornamental stone) Flat surface of a semifinished product without finished edges and obtained by sawing or cutting disks

Polymer (Polymer; Polymer matrix composites; Structural adhesives) Macromolecules (large molecules) consisting of chains of small identical molecules, monomers, which are chemically linked together. [Glossary of basic terms in polymer science—IUPAC Recommendations 1996]

Polymer alloys (Polymer) Polymer blends thermodynamically immiscible, visually homogeneous, with a controlled morphology in a reproducible manner. The control of morphology is usually achieved by the use of “compatibilizers” that stabilize the interfaces

Polymer mixtures (Polymer) Mixtures of chains of at least two different polymers (see *polymer*)

Polymer network (Polymer) Network formed by polymer chains; network nodes are designated by cross-linking points

Polymeric biomaterials (Polymer) Polymer used as biomaterials (which can be in direct contact with living tissues without adverse effects) (see *polymer*)

Polymeric fiber (Polymer) Synthetic fiber produced from thermoplastic polymers of high molecular weight, in which a high degree of crystallinity was induced by suitable processing methods (spinning, drawing by draw rolls, etc.)

Polymerization (Polymer; Polymer matrix composites) Chemical reaction leading to the formation and growth of macromolecular chains from smaller molecules (monomers) or smaller chains formed by a reduced number of monomers (oligomers) also designated prepolymers (see monomer, polymer)

Polymerization agent (Polymer matrix composites) Product added to the base resin in small amounts to induce polymerization reactions

Porosity (Cork) Area occupied by lenticular channels, measured by flat cut

Porosity (Plaster; Renders) (Ornamental stone) Ratio between the volume of pores and/or interstices and the material's total volume, usually expressed as a percentage

Pot life, Working life (Structural adhesives) Period of time during which an adhesive, prepared for application, can be used [NP 3672:1990]

Pourbaix diagram (Corrosion) Graphical representation of the equilibrium potential of the various species of a metal as a function of pH. It allows defining areas of immunity, corrosion, and passivation

Pozzolan (Hydraulic binders; Concrete) Siliceous or aluminosilicate compounds that react with water in the presence of calcium hydroxide—liberated upon cement hydration—and forming additional hydrated calcium silicates and aluminates. For example, natural, pozzolan, fly ash, and silica fume

Precast concrete product (Concrete) Concrete product cast and cured in a place other than the final location of use (factory produced or site manufactured)

Pre-dosed mortar (Plaster; Render) Mortars whose components are dosed at the plant and supplied at work, where they are mixed (see mortar)

Preparation (Cork) Sorting, classification, boiling, cutting of extracted cork

Prepolymer (Polymer) Chains consisting of a small number of monomers (oligomers) that are to be subsequently polymerized (see *monomer*, *polymer*, *polymerization*)

Preservative (Wood) Substance or mixture of chemicals that, once adequately applied, prevent or hinder for a certain period of time the action by some or several organisms capable of destroying or affecting wood

Preservative treatment (Wood) Treatment with a product that aims to increase the resistance of wood to biological alterations

Pressed mud (or sludge) (Ornamental stone) Product (concentrated slurry) resulting from the pressing filter

Primer (Organic coatings) Organic layer applied directly onto a substrate to improve adhesion and/or durability of the painted system

Primer (Structural adhesives) Coating applied to a substrate, prior to the application of an adhesive, to improve adhesion and/or durability of the bond [NP 3672:1990]

Printed glass (Glass) Float glass, colorless or colored, printed with a motif on one side. The printed glass is obtained by drawing and rolling right after the float chamber (offline). It is in the rolling step that the engraving of the motif (present on one of the working rolls) occurs (class of Decorated Glass)

Producer (Concrete) Person or entity that produces fresh concrete

Prospecting (Ornamental stone) Geological and mining work for recognizing the economic value of a reservoir or a mining region

Pultrusion (Polymer matrix composites) Continuous process for manufacturing composite materials of constant cross section, wherein the reinforcing fibers are pulled to the interior of a heated mold with the shape required to be produced and impregnated (either before or simultaneously) by the polymer matrix

Pumice (Ornamental stone) Eruptive or magmatic rock with vitreous texture, with low density, also known as pomito, used to polish or clean and in some regions is used as a construction material for coverings and external paving

Q

Quality assurance (Structural adhesives) All planned and systematic actions necessary to ensure that the final product will perform the intended function

Quality control (Structural adhesives) Activities related to the characteristics, methods and procedures of materials to monitor the compliance of predetermined quantitative and qualitative criteria

Quartzite (Ornamental stone) Metamorphic rock comprised of quartz grains bound together by a siliceous cement

R

Random copolymer (Polymer) Copolymer wherein the constituent monomers are randomly distributed in the chain (see copolymer)

Ready-mix concrete (Concrete) Concrete delivered to the user in a fresh state. According to NP EN 206-1, the following are also considered ready-mix concretes:(1) concrete produced outside the construction site by the user, (2) concrete produced in the construction site, but not by user (see concrete)

Ready-mix mortar (Plaster; Render) Mortar dosed and mixed in plant (see mortar)

Real dimension (Ornamental stone) Any of the dimensions of a slab obtained by direct measurement

Reduction (Corrosion) Electrochemical reaction in which a chemical species gains electrons

Regranulates (Cork) Granules obtained by grinding, milling, or crushing of agglomerated cork

Reheating (Glass) Mandatory cooling process after forming (unitary operation), in which the glass is subjected to a slow and controlled cooling in order to reduce internal stresses

Reinforcement (Plaster; Render, Polymer; Polymer matrix composites, Concrete) Products that are added to the matrix (resin, mortar, plaster, etc.) with the aim of improving mechanical properties (glass fibers, carbon fibers, Kevlar fibers, among others); steel rebars introduced into the concrete to enhance the tensile strength to the composite

Resilience (Polymer) Material's ability to externally return the elastic deformation energy stored during deformation

Resin (Polymer; Polymer matrix composites; Structural adhesives) In the narrow sense, it means a viscous liquid exuded by various plants (particularly conifers) which solidifies in the presence of air. In a broad sense, it is a solid, semisolid or liquid, amorphous, thermoplastic, or thermosetting organic substance, which is a poor conductor of electricity, generally insoluble in water but, under specific conditions, soluble in certain organic solvents or water. They can be natural, artificial, or synthetic [NP 3672:1990]

Resin (synthetic; thermosetting) (Polymer; Polymer matrix composites) Synthetic resin obtained by a polymerization chemical reaction, which results in a (cross-linking) three-dimensional molecular structure with cross-links, complex and partially amorphous; as a result of its irreversible nature, thermosetting resin, once cured, cannot be reprocessed (see *resin*)

Resin (synthetic; thermoplastic) (polymer; polymer matrix composites) Plastic resin is an utilitarian name for the "compound" which feeds the polymer processing units (extrusion, injection, thermoforming, etc.); it includes the "pure" polymer, additives (processing aids, plasticizers, antioxidants, pigments, colorants, anti-foaming agents, antistatic agents, etc.), fillers, and reinforcements. The "formulation" of thermoplastics before processing is currently named compounding: resins are compounded thermoplastic polymers (see resin)

Resistance to segregation (Concrete) Ability of concrete to remain homogeneous while in the fresh state

Resistance to wear by abrasion (Ornamental stone) Physical and mechanical characteristic assessing the degree or strength in a rock to breakdown, caused by all sorts of materials with which it is in contact

Rest potential (Corrosion) The same as (see *corrosion potential*)

Retarder (Plaster; Render) Adjuvant that inhibits the onset of the setting up

Rheology (Concrete) Science that studies the deformation and flow of matter, describing the relationships between stress, deformation, deformation rate and time

Rigid pavement (Binders and bituminous materials) Pavement with top layer performed in cement concrete

Riser (Ornamental stone) Riser background strip, perpendicular to the surface of the riser

Roughness (Plaster; Render) Characteristic of surface texture in a mortar

Rubber (Structural adhesives) Raw material, natural or synthetic elastic polymer (elastomer) which forms the basis of the compound used in many rubber products. In products, family of polymeric materials which are flexible and elastic; rubber can be substantially deformed under stress, but recovers quickly to near its original shape when the stress is removed; it is usually made from a mixture of materials (solid or liquid); and in most products the base polymer is cross-linked by either chemical or physical links [ISO 1382:2012]

S

Sacrificial anode (Corrosion) Active metal used as an anode in cathodic protection, corroding or dissolving over time

Safety glass (Glass) Class of glass with a safety/protection performance regarding property, spaces, or persons (Laminate glass, Tempered glass, and Fire-retarding glass are included)

Sandblasted or shot blasting (Ornamental stone) Surface finishing, etching or the like using sand, steel grit, or iron

Sapwood (Wood) Part of the xylem (wood) that in the standing tree contains living cells and leads the crude sap. The sapwood is usually lighter/paler than the heartwood but not always clearly distinguishable from this

Schistose rock (Ornamental stone) Rock that has minerals with an arrangement in parallel layers, e.g., slate, schist

Scrap (Cork) Reproduction cork with inferior quality, incapable of further use in the production of natural stoppers cork (see cork)

Screen-printed glass (Glass) Float glass decorated by screen printing technique. The frit is applied serigraphically in three distinct patterns—dots, lines, or full coverage. Depending on the standard, the end product is transparent, translucent, or opaque (class of Decorated Glass)

Sealant (Structural adhesives) Adhesive material, used to fill gaps where movement can occur in service and which, when set, has elastic properties. The term "sealant" is also used for a material filling a void against the ingress or egress of a fluid under pressure [EN 923:2005 + A1:2008]

Seals (Polymer) Used in isolating one or more components (or a determined region of space) preventing penetration of liquids or gases in the region to be isolated. They play no structural function, beyond that which can directly result from the isolation needs

Selective leaching (Corrosion) Preferential dissolution of one constituent element of an alloy (see corrosion)

Self-Cleaning glass (Glass) Glass with a surface coating bearing hydrophilic or photocatalytic properties, giving it self-sufficiency when it comes to cleaning, reducing maintenance costs of buildings (class of Coated Glass)

Self-healing (Nanomaterials) Property of a system or device which has the ability to detect faults and make the necessary adjustments to repair them without the need for human intervention

Service class (Wood) Class established according to the environmental conditions to which the structure, or part of it is exposed, intended to derive timber design stresses and allow calculation of deformations in these environmental conditions

Setting up (Concrete) Progressive loss of plasticity of the water-cement mixture

Shaving (Cork) Dry and hard outer part of cork consisting of dead tissues in parts of the cork oak previously subjected to extraction and that are externally adherent to the new suberous tissue formed

Shear strength (Plaster; Render) Resistance determined by the application of a force exerted parallel to the plane of adhesion

Sheets (Cork) Rectangular pieces with a thickness between 1 and 5 mm, resulting from the flat cut of cork blocks

Shelf life; Storage life (Structural adhesives) Time interval during which the adhesive retains intact its initial characteristics under certain environmental conditions [NP 3672:1990]

Shipping-dry wood (Cork) Wood having a moisture content sufficiently low to prevent the action of chromogenic molds and fungi or rot during its transport (usually water content below 20 %)

Shock resistance (Ornamental stone) Physical and mechanical characteristic which assesses the resistance to impact. It uses a standard methodology in which a previously controlled mass is dropped in the rock's surface from initially set heights until a fracture becomes apparent

Shrinkage (Plaster; Render; Concrete; Wood) Dimensional reduction of an element relative to its original size. Shrinkage occurs during, e.g., the hardening of a mortar or by reduction of moisture content of wood

Shrinkage Coefficient (Wood) Shrinkage in a given anatomical direction of wood due to a reduction of 1 % of its moisture content, in the range between 0 % and the fiber saturation point

Single blade machine (Ornamental stone) Equipment that has only one blade, which is used for primary sawing and block trimming

Sizings (Polymer matrix composites) Chemical treatment apply to fibers' surfaces in order to enhance their surface resistance and protect them from damage during the manufacturing process

Slab (Ornamental stone) Any element in natural stone used as a paving material whose nominal width usually exceeds 150 mm and, generally, is twice the thickness

Sleeks (or lines) (Ornamental stone) Thin inclined joints almost imperceptible on a stone

Slip resistance (Ornamental stone) Friction between the floor and a friction tester in a sliding test under well-defined circumstances and in accordance with the applicable standard

Slubbed (Ornamental stone) Surface finish via a thermal change that alters and modifies the structure of the grains and pores of the stone giving it a rough visual aspect; the process can be done manually by torch or by automatic machine

Slurry seal (asphalt slurry) (Ligand and bituminous materials) Surface treatment consisting in situ application of a mixture of mineral aggregate, bituminous emulsion, and additives

Soft (Cork) Agglomerate consisting of cork, usually with a density <350 kg/m^3 and used for decorative or special purposes

Softwood (Wood) Wood from trees of the botanical group of Gymnosperms, conifers

Soleto (Ornamental stone) Thin slate plate

Solid materials (Ornamental stone) Products that usually have a thickness greater than 100 mm

Specification of concrete (Concrete) Final compilation of documented technical requirements given to the producer in terms of performance or composition

Static fatigue (Polymer) Test whereby the breaking strength of a test specimen subjected to a constant load, i.e., under flow conditions, is measured

Steel (Steel) Alloy primarily constituted of iron and carbon (2 wt%). It may contain other metallic elements

Strands (or beams) (Polymer matrix composites) Geometry of reinforcing fibers materialized by sets of quasi-parallel continuous filaments, non-twisted (rovings) or twisted (yarns)

Strength class (Wood) Result of the classification of structural timber based on particular values of its mechanical properties and density

Structural adhesive (Structural adhesives) Adhesive involved in the integrity of a structure that is able to withstand high loads without failure over extended periods [NP 3672:1990] (see adhesive)

Stress corrosion cracking (Corrosion) Deterioration of the material due to the synergic action of applied or residual tension and a corrosive environment. The fracture occurs in the time interval shorter than expected from the sum of isolated actions of stress and of the aggressive environment (see corrosion)

Stress relief (Polymer) Test which measures the time response to a degree of mechanical deformation

Stripe (Ornamental stone) Narrow mineral body in relation to other dimensions, which runs across some rocks

Stripping or extraction (Cork) Periodic extraction of the bark (cork) of the trunk and branches of the live cork oak

Structural adhesives (Structural adhesives) Adhesive forming bonds capable of sustaining in a structure a specified strength for a defined long period of time [EN923:2005 + A1:2008]

Substrate, Adherend (Structural adhesives) Material (surface) that is, or is intended to be, held to another material by an adhesive [NP 3672:1990]

Superplasticizer (Plaster; Render; Concrete) Admixture that allows a strong reduction of the amount of mixing water without affecting consistency, or allowing an increase in fluidity, without affecting the amount of mixing water, or both effects simultaneously

Supplementary cementitious materials (Hydraulic binders) See *cementitious materials*

Support (Plaster; Render) Surface on which the mortar is applied

Surface coating (Bituminous binders and materials) Surface treatment consisting in successively applying at least one layer of binder and at least one layer of gravel

Surface tension (Structural adhesives) Reversible work required to create a unit area on the surface of the material

Swelling (Wood) Increase in size/volume of wood due to the increase of its moisture content

T

Tack coat (Binders and bituminous materials) Application of a bituminous film, intended to ensure the connection between two layers, so as to improve thickness. It can sometimes be done by applying gravel

Tempered glass (Glass) Safety glass treated chemically or thermally to improve its mechanical performance. Tempered glass is two to five times more resistant than ordinary glass (float glass simply annealed). Tempered glass fractures into small pieces of not sharp edges, preventing injury to persons (class of safety glass)

Tensile strength (Plaster; Renders) Capacity of the mortar to withstand a tensile force applied perpendicular to its surface

Thermal dynamic mechanic analysis (Polymer) Dynamic-mechanical tests where the temperature varies with time at a constant rate (heating or cooling)

Thermal insulation material (Plaster; Renders) Low heat transfer coefficient material that makes it possible to reduce heat transfer between two media

Thermal linear expansion (Ornamental stone) Physical characteristic which evaluates the expansion/shrinkage of the stone by the action of temperature variations

Thermal shock resistance (Ornamental stone) Assesses changes in rocks caused by abrupt alterations in temperature. Usually, the test consists of 20 alternating cycles of heating at 105 °C and immersing in water at 20 °C

Thermoplastic (Polymer) Polymer consisting essentially of linear chains, eventually with some ramifications. When heated, it becomes plastic and can be molded reversibly

Thermoplastic elastomers (Polymer) Are elastomers physically cross-linked through segregation effects. They consist of block copolymers presenting segregation, and constituted by two or more blocks having very different glass temperatures. At low temperature, all blocks are glassy; at high temperatures all blocks become molten and can be processed as thermoplastics. At intermediate temperatures, some blocks are molten and others not; if the microstructure is constituted by a continuous phase of molten blocks, and the glassy blocks are segregated as nodules dispersed in the molten phase, these nodules act as active fillers, chemically bound to the molten subchains, and the material behaves like cross-linked elastomers (see *elastomers*)

Thermoset (Polymer) polymer network obtained by polymerization of multifunctional monomers; each monomer reacts with three or more other monomers, and the final result is a tight network (high mesh number). As the polymerization proceeds, the material hardens irreversibly

Thick cork (Cork) Cork (board) that has a thickness of 18–25 lines (see line)

Thin cork (Cork) Cork (plank) having 9–12 lines (see line)

Thixotropy (Structural adhesives) Decrease of apparent viscosity under shear stress, followed by a gradual recovery when the stress is removed [EN 923:2005 + A1:2008]

Tightness (Ornamental stone) A characteristic of something that is resistant to penetration; does not allow gas exchange

Tile (Cork) Part, usually square or rectangular, for floor or wall covering

Tile (Ornamental stone) Plates or tiles in square or rectangular format, for floor

To age (Ornamental stone) Manufacturing processes which give a visual aspect of the aging stone, either through mechanical, washing, or release processes for chemicals that corrode stones

Topcoat (Organic coatings) Paint, varnish, or lacquer that can be used as a final layer in a paint system

Top face (Ornamental stone) Slab surface within view, when applied (see face)

Total dosage of water (Concrete) Sum of the amount of water introduced into the mixer with the water present inside and on the surface of the aggregates, in the additions and admixtures used as a suspension and with the added ice or steam heating

Transversal deformability (Renders; Plaster) Flexion recorded at the center of a mortar specimen of mortar subjected to a load at three points.

Travertine (Ornamental stone) Sedimentary carbonate rock of chemical origin, in which the limestone is distributed in layers in a compact set

Trimming (Ornamental stone) Face milling and trimming of blocks or pieces of stone before manufacture

Thermal modification (Wood) Treatment of wood at elevated temperatures (above 150 °C) in the absence of oxygen. The process changes the chemical composition of wood, and in particular the hemicellulose components

Thermal tempering (Glass) Ordinary glass (simply annealed glass) is subjected to a heat treatment where it is reheated to the softening point (~680 °C for soda-lime silicate glasses), and then rapidly cooled. Minimum surface pressure is 69 MPa. For the temper to be considered effective, after fracture the area of the ten biggest pieces of glass should not exceed 6.5 cm^2. If, after heat treatment, cooling is slow, the glass will become only two times stronger than ordinary glass and if it breaks, it will do so in linear fragments with an area higher than that of tempered glass, but still easy to keep in the support (thermally toughened glass). Surface compression is then between 21 and 69 MPa

U

Unglazed tiles (Ceramic) Tiles that receive no superficial vitreous coating. They are classified as unglazed (UGL) (see *ceramic tiles*)

Uniform corrosion (Corrosion) Corrosion that develops at the same rate over the entire metal surface (as opposed to forms of localized corrosion) (see *corrosion*)

Use class (Wood) Scenario with higher or lower probability of an attack to wood by the main biological agents capable of degradation (taking into account their preferred development conditions) that can be associated to the various environments of wood application in construction

V

Vascular cambium (Wood) Tissue forming a narrow bed of meristematic cells that in the living tree generates phloem cells to the outside and xylem cells (wood) towards the interior

Ventilated façade (Ornamental stone) External application of stone to walls of buildings by a system of metal anchorage by which the latter receive ventilation (natural or forced) (see front)

Verification (Concrete) Confirmation by examination of objective evidence that specified requirements have been satisfied

Visual strength grade (Wood) Result of sorting timbers by means of visual inspection (according to set limits for defects and singularities) into a grade to which characteristic values of strength, stiffness, and density may be allocated

Vitreous relaxation temperature or vitreous glass temperature, T_g (Glass; Structural adhesives; Polymer) Characteristic temperature of an amorphous material (glass, polymer), below which it is no longer in thermodynamic equilibrium; as a result, during cooling, a sharp increase in viscosity (glass) or elastic moduli (polymer) in the value of several orders of magnitude can be observed (103, 104, or more). In addition to the structure and chemical composition, T_g depends on the cooling rate and the thermal history of the sample

Volcanic rock (Ornamental stone) Class of igneous rocks that leaked or were ejected to the earth's surface or close to it

Vulcanization (Polymer) Elastomer cross-linking process (natural rubber and others) with the use of sulfur. In the broadest sense, it is sometimes used to refer to the general process of elastomer cross-linking, even without using sulfur

W

Waiting time (Structural adhesives) Minimum time required between application of the adhesive and the union of substrates [NP 3672:1990]

Wane (Wood) Portion of the original surface of the trunk, with or without bark, present in a piece of sawn timber

Warping (Wood) Distortion of a timber piece resulting from the sawing, drying, or storage process

Washing with acid (Ornamental stone) Process used to give an antique look to rocks

Water absorption (Ceramic) Weight percentage of absorbed water according to EN ISO 10545-3 Norm

Water jet (Ornamental stone) Cutting process using water at high pressure

Water retention (Plaster; Render) Ability of a fresh hydraulic mortar to retain mixing water when exposed to the support's suction, allowing its normal hardening

Water vapor permeability (Plaster; Render) Flow of water vapor that traverses mortar, under conditions of equilibrium, per surface area and vapor pressure unit

Water/cement ratio (Concrete) Mass ratio between the effective water content and cement content in fresh concrete

Wear layer (Binders and bituminous materials) Top layer of a pavement in direct contact with traffic

Wedding veil (surface veil) (Polymer matrix composites) Mat with reduced thickness with short fibers arranged randomly usually applied to the surface of the laminate

Wet cutting (Ornamental stone) Water- or liquid-based sawing or cutting process

Wet strength (Ceramic) Resistance of a glued joint determined immediately after removal of a liquid in which it has been immersed under specified conditions [NP 3672:1990]

Wet strength (Structural adhesives) Strength of an adhesive joint determined immediately after removal from a liquid in which it has been immersed under specified conditions [NP 3672:1990]

Wettability (Structural adhesives) Ability of a liquid (adhesive) to spread on a specific solid surface [EN 923:2005 + A1:2008]

Wetting power or wettability (Plaster; Render) Ability of a fresh mortar to wet the associated support or material, facilitating adherence

Wired glass (Glass) Glass that incorporates a square metal mesh. If fractured, it retains glassy fragments of sharp edges, preventing its fall, potential cause for accident, while continuing to act as a barrier to the entry of people or objects (class of safety glass)

Workability (Plaster; Render; Concrete) Greater or lesser ease with which a concrete or mortar is transported, placed, consolidated, and hardened, maintaining its homogeneity during these operations

Working region (Glass) Range of viscosities (103 and 106.5 Pa·s) where it is possible to mould the glass

Weld decay (Corrosion) Localized corrosion of certain metals (particularly austenitic stainless steel) in areas near the weld beads (see corrosion, intergranular corrosion)

Wood modification (Wood) Process whereby permanent changes occur in the chemical structure of the chemical components, so altering behavior and performance

X

Xylem/Wood (Wood) Cellulosic matter lying between the pith and the bark of a tree

Y

Yield stress (Concrete) Minimum tension to start the flow of concrete

Yellow spot (Cork) Yellow or light gray stain, sometimes with mildew odor, which thrives in moist environments from the back to the belly of the board, caused by a fungus. It is a defect that excludes the use of cork for cork stoppers (see *cork*)

Contents

1 Hydraulic Binders

Carla Costa

Abstract

Hydraulic binders play a vital role in the economic and social development because they are essential components of concrete, the most widely used construction material. Nowadays, Portland cement is the most predominantly used hydraulic binder due to its properties and widespread availability. Cement manufacture consumes large amount of non-renewable raw materials and energy, and it is a carbon-intensive process. Many efforts are, therefore, being undertaken towards the developing "greener" hydraulic binders. Concomitantly, binders must also correspond to market demand in terms of performance and aesthetic as well as fulfill mandatory regulations. In order to pursue these goals, different approaches have been followed including the improvement of the cement manufacturing process, production of blended cements, and testing innovative hydraulic binders with a different chemistry. This chapter presents a brief history of hydraulic binder's discovery and use as well as the environmental and economic context of cement industry. It, then, describes the chemistry and properties of currently most used hydraulic binders—common cements and hydraulic limes—and that of the more promising binders for future applications, namely special Portland cements, aluminous cements, calcium sulfoaluminate cements, and alkali-activated cements.

Keywords

Hydraulic binders • Common cements • Hydraulic lime binders • Aluminous cements • Calcium sulfoaluminate cements • Alkali-activated cements

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M.C. Gonçalves, F. Margarido (eds.), *Materials for Construction and Civil Engineering*, DOI 10.1007/978-3-319-08236-3_1

1.1 Introduction

The expression *binder material* designates substances that harden independently and bind other solid materials, conferring cohesion and resistance to the system [1]. Binders can *agglomerate* solids or *join them* along their contact surfaces. This expression comprises construction materials of distinct nature and properties, with different applications and economic importance.

Hydraulic binders are substances that chemically react with water, by converting the water-binder system with plastic consistency into a solid matrix with the ability to agglomerate other solid materials. This hardening process takes place spontaneously at room temperature, both underwater and exposed to wet weather.

Table 1.1 presents the classification of binder materials, according to their affinity for water, and presents examples of materials and their applications.

Hydraulic binders, particularly cement, are a commodity in mankind's economic and social development, due to their relevant role in the constitution of concrete,[1] which is the most currently used material in the world.

Table 1.1 Classification of binder materials, according to their affinity for water

Binder	Affinity for water		Examples	
			Materials	Applications
	Hydrophile	*Aerial*	• Plaster • Air lime	• Ceramic • Mortar
	Solid inorganic substance that chemically reacts with water	• Sets and hardens in contact with air. Hardened material is not stable in water		
		Hydraulic	• Cement • Hydraulic limes • Blast furnace slag	• Concrete • Mortar • Grout
		• Sets and hardens both in contact with air and underwater. Hardened material retains stability and resistance in both environments		
	Hydrophobe		• Hydrocarbon (bitumen, tar) • Polymer (glues, resin)	• Waterproofing • Flooring • Surface coating
	Organic substance that is a viscous liquid or a colloid which hardens by heat treatment, solvent evaporation, or chemical reaction between the components. Water does not interfere with the hardening process and the hardened material repels it			

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[1] *Concrete* is a composite material composed of a hydraulic binder, inert aggregates (fine and coarse), water and, sometimes, additives. When the mixture contains only fine aggregates (with maximum dimension up to 4 mm), the resulting material is a mortar. If no aggregates are added, the resulting material is a grout. In this chapter, these construction materials—concrete, mortar, and grout—are indiscriminately referred to as "cement-based materials."

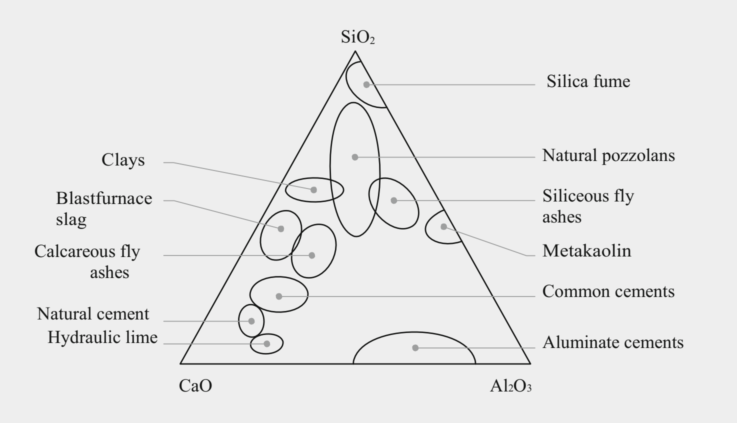

Fig. 1.1 Ternary CaO–SiO_2–Al_2O_3 phase diagram showing the composition of the hydraulic binders and other often-associated materials

Hydraulic binders are mainly composed of silica (SiO_2), alumina (Al_2O_3), and lime (CaO). The specific chemico-mineralogical composition of each binder determines its reactivity with water, and thus its binding properties. Figure 1.1 schematically presents the composition of the hydraulic binders and other materials that are often associated with them (and that will be examined in this chapter) in the CaO–SiO_2–Al_2O_3 phase diagram.

Hydraulic binders are classified according to their reactivity, in:

- *Active*, if they have the ability to react spontaneously with water (e.g., hydraulic lime, cement)
- *Latent*, if they require the presence of a suitable alkali activator (Sect. 1.4.2.1) to present a significant hydration extent (e.g., blast furnace slag)

Combined active and latent hydraulic binders originate *composite hydraulic binders* [2]. There are other materials that, in spite of not spontaneously reacting with water, acquire hydraulic properties in the presence of calcium hydroxide. These materials are called *pozzolans* or *pozzolanic materials* (Sect. 1.4.2.1) and can be both of natural origin or industrial by-products such as fly ash and silica fume.

The geographic abundance [3] of limestone and clay, which are the raw materials for the manufacture of hydraulic binders has certainly determined the beginning of their use as building materials since ancient times. This has also led to the discovery of their hydraulic properties, albeit in a semi-empirical way.

The first identified hydraulic binder—designated by *hydraulic lime*—was obtained from heat treatment (calcination) at about 1,000 °C of impure limestone,[2]

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[2] The thermal activation of limestone containing impurities below 5 % gives rise to a binder product without hydraulic properties, which is called air lime.

containing from 6.5 to 20 % of clay (Sect. 1.5.1). This binder was the precursor of another hydraulic binder designated by *natural cement*. This binder is produced from limestone containing higher clay content (between 20 and 40 %) activated at higher temperatures (between 1,000 and 1,300 °C) [4, 5] leading to improved mechanical properties [6]. In fact, the term *cement* was introduced to designate hydraulic binders whose mortars showed higher strength than those obtained from hydraulic lime [7].

Technological advances in the cement manufacturing, namely using calcination temperatures higher than 1,300 °C led to the developments of the Portland artificial cements (Sect. 1.4) with even improved mechanical properties.

Portland cement has a very expressive current global consumption of 2,800 million tons in 2007, which is equivalent to about 400 kg/per capita [8] and is still the most predominant hydraulic binder used in construction. Moreover, it is possible to establish a direct relationship between the consumption of cement and a country's standard of living [9]. The widespread use of cement in the future still seems unavoidable. In fact, it is estimated a significant increase in the cement consumption worldwide, in the coming years, despite the slowdown in its exponential consumption growth in the latest years due the current global crisis.

However, from an environmental perspective, the best available technology for the production of Portland cement is inherently vulnerable, particularly considering CO_2 emissions (Sect. 1.3). Current sustainability concerns include greater consideration for environmental impacts and for long-term consequences of constructive interventions, as well as the need for a rational management of limited material and financial resources. It is, therefore, urgent to develop innovative hydraulic binders.

Future binders should: (1) have an environmentally optimized production process, using smaller amounts of natural raw materials and fuel, as well as having lower CO_2 emissions, (2) use by-products from other industries, thus contributing to the mitigation and valorization of solid wastes, (3) have higher durability, (4) have a less costly maintenance, and (5) be more diversified and technologically oriented to the market requirements, concerning aesthetics and multi-functionality.

The new twenty-first-century approach in regard to construction materials foresees that cement will be one of a wide range of substances, with or without hydraulic properties, synthesized and employed by the cement industry. This will correspond to a paradigm shift: the "cement industry" will transform itself in the "hydraulic binder's industry" [9].

Understanding hydraulic binders at their fundamental level—to which the present chapter aims to contribute—provides: (1) *researchers* with scientific basis to support the development of novel, sustainable and inexpensive materials that are able to meet their functional requirements during their whole service life, and (2) *engineers and architects* with knowledge to support more correct decisions on design, execution, and site maintenance considering ecological and socio-economic costs of their interventions.

This chapter starts with an overview of the hydraulic binder's historical evolution (Sect. 1.2) followed by the economic and environmental context of their production industry (Sect. 1.3). Thereafter, it describes the hydraulic binders with a more generalized use—namely, common cements (Sect. 1.4), hydraulic limes (Sect. 1.5.1), and special Portland cements (Sect. 1.5.2), and finally, presents the most promising binders for the future—namely, aluminous cements, calcium sulfoaluminate cements, and alkali-activated cements (Sects. 1.5.3–1.5.5).

1.2 History of Hydraulic Binders

The early use of natural inorganic materials in construction dates back to the Neolithic period (8000–2500 BC) [5, 10]. The discovery of hydraulic binding properties of calcareous materials must have been fortuitous. Later, their application became generalized, with remarkable quality, in the Roman Empire. Many of the constructions where they were used by the Romans still remain in good condition. However, with the fall of this Empire, the use of those binders was interrupted and the knowledge of its production process was lost.

In the eighteenth century, the interest for these materials reappeared. Systematic studies made henceforth and the subsequent technological progress has granted their chronological evolution. Calcareous materials used as hydraulic binders evolved from hydraulic limestone to natural cement and finally to artificial cement. The chemical composition of all these hydraulic binders is not significantly different, as evidenced by the schematic representation in the $CaO–SiO_2–Al_2O_3$ phase diagram (Fig. 1.1). Their differences are essentially found at the mineralogical level, due to raw materials composition and production process. There are, however, some important differences: hydraulic lime as high levels of free calcium oxide (CaO); natural cements contain significant quantities of calcium silicates, especially dicalcium silicate ($2CaO{\cdot}SiO_2$) and contemporary artificial cements present a greater amount of tricalcium silicate ($3CaO{\cdot}SiO_2$) in relation to dicalcium silicate [11]. The hydraulicity of these binders is related to the amount of calcium combined with other constituents, namely in the form of silicate [6].

Table 1.2 presents the most significant events in the history of hydraulic binder's evolution.

1.3 Hydraulic Binder's Industry Context

This section addresses the economic and environmental importance of the hydraulic binder's industry. As already mentioned, more than 95 % of hydraulic binders consumed worldwide are common cements [12–17]. Therefore, the only data available concerning the production of common cements may be considered as good indicators of the hydraulic binder's industry context.

Figure 1.2 shows that the global cement production has had an exponential growth from ten million tons in 1990 to 2,814 million tons in 2007 [5, 8]. Moreover, the cement production, which became more significant after the 1960s, more than duplicated in the last two decades. Considering the current global economic crisis, this growth trend is expected to slow down. However, a significant overall growth

Table 1.2 Chronology of the most significant events in the international history of the hydraulic binder's evolution of [5, 6, 9, 20, 32]

Year	Event
2500 BC	*Egyptians*: used mortars made with a binder obtained by gypsum calcination in, for example, the Pyramids of Giza
800 BC	*Greeks and Cretences*: used slaked lime mortars with sand
300–500 BC	*Romans*: used mortars made with volcanic origin soils, grinded lime, and sand. These mortars besides having higher strength were able to harden in water. Since the best volcanic soil for this purpose was found near the Italian town of Pozzuoli, this soil was designated as *pozzolan*. Later on, this designation included other substances with similar cementitious properties. These mortars were used, for example, in the construction of the Patheon (127 BC) and the Coliseum (82 BC), in Rome, and the structures still stand today
Middle Ages	In the Middle Ages, the knowledge to produce high-quality mortars was lost, and its use was discontinued
1756	*John Smeaton* (English): identified and (re)used the hydraulic properties of lime mixed with pozzolans, for the first time after the Roman Empire, when was rebuilding the Eddystone Lighthouse in Cornwall
1796	*James Parker* (English): patented the discovery of *natural hydraulic cement* production from calcined impure limestone containing lime
1812–1813	*Louis Vicat* (*French*): established the principle of *artificial hydraulic lime* manufacture from synthetic mixtures of limestone and clay
1824	*Joseph Aspdin* (*English*): registered the first artificial cement patent, which he named "Portland cement," by analogy with a stone quarried on the English Island of Portland, which had a similar color, and reputation for quality and durability. This patented cement was produced by burning limestone with finely ground clay in a kiln until the occurrence of CO_2 emissions. This synthesized product was then ground into finished cement with higher mechanical strength than previously prepared binders. The cements currently referred to by the same name are technologically more evolved
1877	The association of German cement manufacturers, Verein Deutscher Zementwerke (VDZ), published the first Cement Standard to provide cement quality guarantee
1887 and 1897	Le Chatelier (French) and Törnebohm (Swedish): began the first scientific studies in the field of cement chemistry
1900	• The first rotary kiln to produce cement was built in Essex, England. Inside this kiln, the material's temperature profile allows the formation of mineralogical different products that contribute to increase the strength of the final materials. This kiln also allows the production of more homogeneous cements and on a larger scale
	• *Pierre Giron* (*French*, working in the USA) added, for the first time, gypsum to cement during the final grinding, which resulted in a significant development of the cement's chemical composition and allowed the optimization of cement hardening
Twentieth century	Mechanical properties of cement were consolidated by rapid scientific and technological developments. The most relevant factors were: (1) increase of the tricalcium silicate/dicalcium silicate ratio (although the content in silicates remained unchanged), (2) increase of cement particle's fineness,

(continued)

Table 1.2 (continued)

Year	Event
	(3) development of organic additives, including superplasticizers (synthetic polymers with exceptional ability to disperse cement particles). These changes lead to a 4–5 times increase in the strength of the concrete prepared with cement (Sect. 1.4.1)
2000	The European Committee for Standardization (CEN) published the first standard—EN 197-1:2000—to harmonize the quality of common cements among the member states of the European Union (Sect. 1.4) and to eliminate technical barriers in cement trade

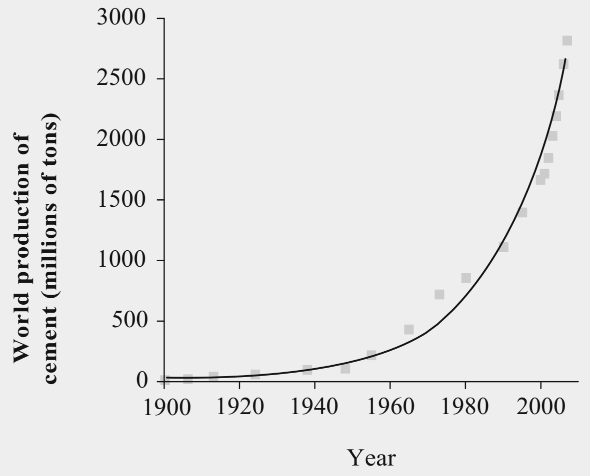

Fig. 1.2 World production of cement [5, 8]

in cement production is still anticipated, at least until the mid-twenty-first century [5, 8, 12].

Such significant values of cement production require that the cement industry addresses its environmental impact in a global context. The major factors contributing for the ecological fragility of this industry are [18, 19]:

- *Consumption of raw materials*: about 1.7 tons per ton of cement produced.
- *Fuel consumption*: about 1.8 GJ per ton of cement produced. This value is relatively low when compared to other building materials, such as iron, which consumes 40 GJ per ton. However, the large amount of cement produced makes this industry responsible for about 2 % of global primary energy consumption and for almost 5 % of global industrial energy consumption.
- *CO_2 emissions*: about 1 ton of CO_2 emission per ton of cement produced. CO_2 sources are mainly the fuel and the decarbonation of limestone. This industry contributes for 5–7 % of global CO_2 anthropogenic emissions.

In this context, opportunities to mitigate the environmental impact of cement industry include: the use of alternative raw materials, namely by-products from other industries; the optimization of the plants energy consumption; the reduction of limestone proportion in cement products as well as the use of industrial by-products as partial surrogates of the cement itself. Similarly, it is necessary to promote improvements in cement durability in order to increase their service life and thus minimize the need for replacement as well as to develop other "greener" hydraulic binders.

1.4 Common Cements

Nowadays, a wide variety of cements is produced in almost all countries of the world. Raw materials, mainly clay and limestone, are rigorously proportioned and heated to about 1,450 °C to form a product consisting of calcium silicates and aluminates, called "clinker." This product, is finely ground with gypsum to produce the "Portland cement." The use of cementitious materials or minerals either as partial replacement for clinker or as additions to cement produces "blended cements" (Sect. 1.4.2). The current available technology and knowledge ensure the production of cements with a statistically homogeneous and reproducible composition.

The terms "clinker" and "Portland cement" have a widespread acceptance. However, there are a number of other terms, namely to designate blended cements and other hydraulic binders whose definitions are not consensual in scientific and technical literature. This lack of consistency in terminology and in the criteria for the evaluation of materials properties is extensible to quality standards set by different countries, among which there is often no equivalence.

In the European Union, the European Committee for Standardization (CEN[3]) elaborated the standard EN 197-1:2000 [20] which specifies the composition, the requirements (mechanical, physical, chemical, and durability), and the conformity criteria that cements and their constituents must meet to be certified. These cements are designated as "common cements," abbreviated CEM and are classified based on the composition and strength.

Regarding the composition, there are 27 *products* in *common cements* family, grouped into five main types. Cements are always made of clinker and gypsum (Sect. 1.4.1) and, depending on its type, they can also contain the following addition (s): blast furnace slag, silica fume, pozzolans, fly ash, burnt shale,[4] and limestone (Table 1.3). According to the standard EN 197-1:2000, if these additions content is higher than 5 % by mass, they are also considered main constituents (Sect. 1.4.2). When especially selected inorganic materials are added at less than 5 % by mass,

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[3] CEN arises from the French designation "Comité Européan de Normalization."

[4] Silica fume, fly ash, and burnt shale are also pozzolanic materials (or pozzolans). However, the standard EN 197-1:2000 adopts the terminology "pozzolan" for natural pozzolanic materials, with the exception of burnt shale. Silica fume and fly ash have pozzolanic properties but they are industrial by-products, not naturally occurring (Sect. 1.4.2).

Table 1.3 Designation, notation, and composition of the main types of common cements defined in the standard EN 197-1:2000 [20]

Main types	Notation	Composition (%, by mass)	
		Clinker[a] (%)	Other main constituent rather than clinker
Portland cement	CEM I	95–100	
Portland composite cement	CEM II	65–94	Up to 35 % of an addition[b]
Blast furnace cement	CEM III	5–64	36–95 % blast furnace slag[c]
Pozzolanic cement	CEM IV	45–89	11–65 % of pozzolanic materials (of one type or a mixture of several types)[d]
Composite cement	CEM V	20–64	Mixture of: (1) 18–50 % of blast furnace slag and (2) 18–50 % of natural pozzolan and/or fly ash

[a] Content of gypsum in cements composition is not specified by the standard. However, since gypsum is always present (Sect. 1.4.1), it is considered as being included in the percentage set by the standard to the clinker

[b] Considers different subclassifications depending on the addition(s) present on cement constitution

[c] Considers subclassifications depending on the slag content

[d] Considers subclassifications depending on the additions present

they are designated “minor additional constituents” and do not affect cement’s classification. Common cements can also include organic compounds in their constitution which are added to improve the manufacturing process or the cement properties. These compounds shall not exceed 1 %, by mass, of cement.

Common cements are also classified into six reference *strength* classes depending on the value of their compressive strength at 28 days of hydration. Annex I includes a table presenting the correspondence between the designation and notation of common cements with the respective composition and mechanical and physical requirements, as defined in the standard EN 197-1:2000 [20]. Examples of common cements identification are also given.

Figure 1.3 shows the percentage of the different types of common cements produced and sold in the European market over the years. There is a clear progressive decrease in production and sale of cement type CEM I accompanied by an increasing production and sale of blended cements, mainly type CEM II. This change in the type of common cement used is due to the environmental, economic, and technological reasons listed in Sect. 1.4.2.1.

Chemical and mineralogical composition of cements determines the microstructure of the hardened materials and hence their macroscopic properties. The understanding of the correlation between the microstructure and the properties contributes to a proper assessment of the behavior of the cement-based materials throughout their life and service (Sect. 1.4.1.3).

Cement-based materials have a complex microstructural organization, which is highly heterogeneous on local chemico-mineralogical composition. As such, in the

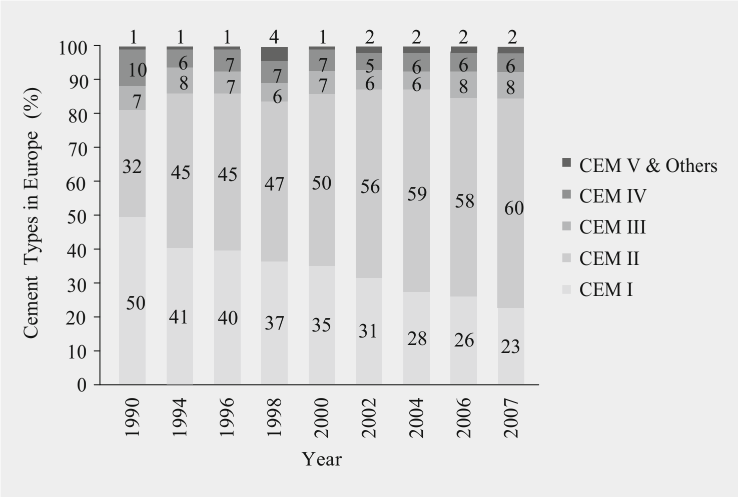

Fig. 1.3 Types of common cements (according to standard EN 197-1:2000) produced and sold in the European market [8]

Table 1.4 Oxides symbols in accordance with the notation used in the cement chemistry

Oxide	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	Na_2O	K_2O	SO_3	CO_2	H_2O
Symbol	C	S	A	F	M	N	K	$\overline{S}$	$\overline{C}$	H

Table 1.5 Abbreviated notation of the main chemical components of cement

Composite	Composition	Abbreviation	Impure phase
Tricalcium silicate	$3CaO \cdot SiO_2$	C_3S	Alite
Dicalcium silicate	$2CaO \cdot SiO_2$	C_2S	Belite
Tricalcium aluminate	$3CaO \cdot Al_2O_3$	C_3A	
Tetracalcium aluminoferrite	$4CaO \cdot Al_2O_3 \cdot Fe_2O_3$	C_4AF	Celite
Calcium hydroxide	$Ca(OH)_2$	CH	Portlandite
Calcium sulfate	$CaSO_4$	$C\overline{S}$	–
Gypsum	$CaSO_4 \cdot 2H_2O$	$C\overline{S}H_2$	–
Calcium silicates hydrated (*variable chemical composition*)	$x CaO \cdot SiO_2 \cdot y\ H_2O$	C-S-H	

domain of the cement chemistry, the compounds are referred to by the use of a simplified notation (different from the usual nomenclature of chemical formulas) in which:

- The chemical elements are expressed in terms of their oxide forms.
- The oxides are represented by the first letter of their chemical formula (Table 1.4).
- The proportion in which the oxides are present in the compound is written in index (Table 1.5).

However, it should be noted that the notation does not mean that the oxides have a separate existence in the structure, i.e., it has no chemical meaning.

1.4.1 Portland Cement

This section addresses the manufacturing process, the composition, the hydration mechanism, and the microstructure–properties correlation of the Portland cement type CEM I, specified in the standard EN 197-1:2001 [20].

1.4.1.1 Manufacturing Process

The physical and chemical phenomena that occur during the cement manufacturing process determine the chemico-mineralogical composition of the final cement product and its compliance with the compulsory specifications. Figure 1.4 shows a scheme of the manufacturing process of Portland cement which main steps are:

- Raw materials preparation
- Clinker production
- Final grinding of clinker with gypsum

Raw Materials Preparation

- Raw materials constituents

  Cement is produced mainly from a mixture of limestone (about 75 %) and clay (about 25 %). Quarried limestone is a rock consisting of calcium carbonate ($CaCO_3$) containing impurities such as silica (SiO_2), clay ($Mx/n[xAl_2O_3{\cdot}SiO_2]{\cdot}zH_2O$),[5] iron oxide ($Fe_2O_3$), and magnesium oxide (MgO) [2].

  To ensure the appropriate chemical composition of the final product, the mixture proportions of these raw materials may require a correction of some chemical elements by adding, small amounts of corrective materials such as quartz and iron ore [21].

  Limestone and clay are extracted from the quarries in blocks with a maximum size of 1–2 m and crushed to reduce their size until 25–200 mm [22]. Thereafter, they are stored into silos equipped with pre-homogenization systems. Good homogeneity of each raw material is essential for final product quality and plant efficiency [22].

- Raw materials blend mill

  The fineness and particle size distribution of the raw materials blend also influence the clinker manufacture process and, hence, the quality of the final product. As such the production of clinker requires that in the raw materials blend, the limestone particles size is less than 125 μm and that the other raw materials particles size is less than 45 μm. Typically, 85 % of the raw materials particles size is less than 90 μm [2, 21, 23].

  The finely ground raw materials blend, known as raw meal, is, then, stored in other silos also equipped with homogenization systems [22] before to proceed for the following step which is the clinker production.

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[5] Clay is a natural hydrated aluminosilicate $Mx/n[xAl_2O_3{\cdot}SiO_2]{\cdot}zH_2O$, wherein M represents metal ions, usually alkali (Na^+, K^+), Mg^{2+}, and Fe^{3+}.

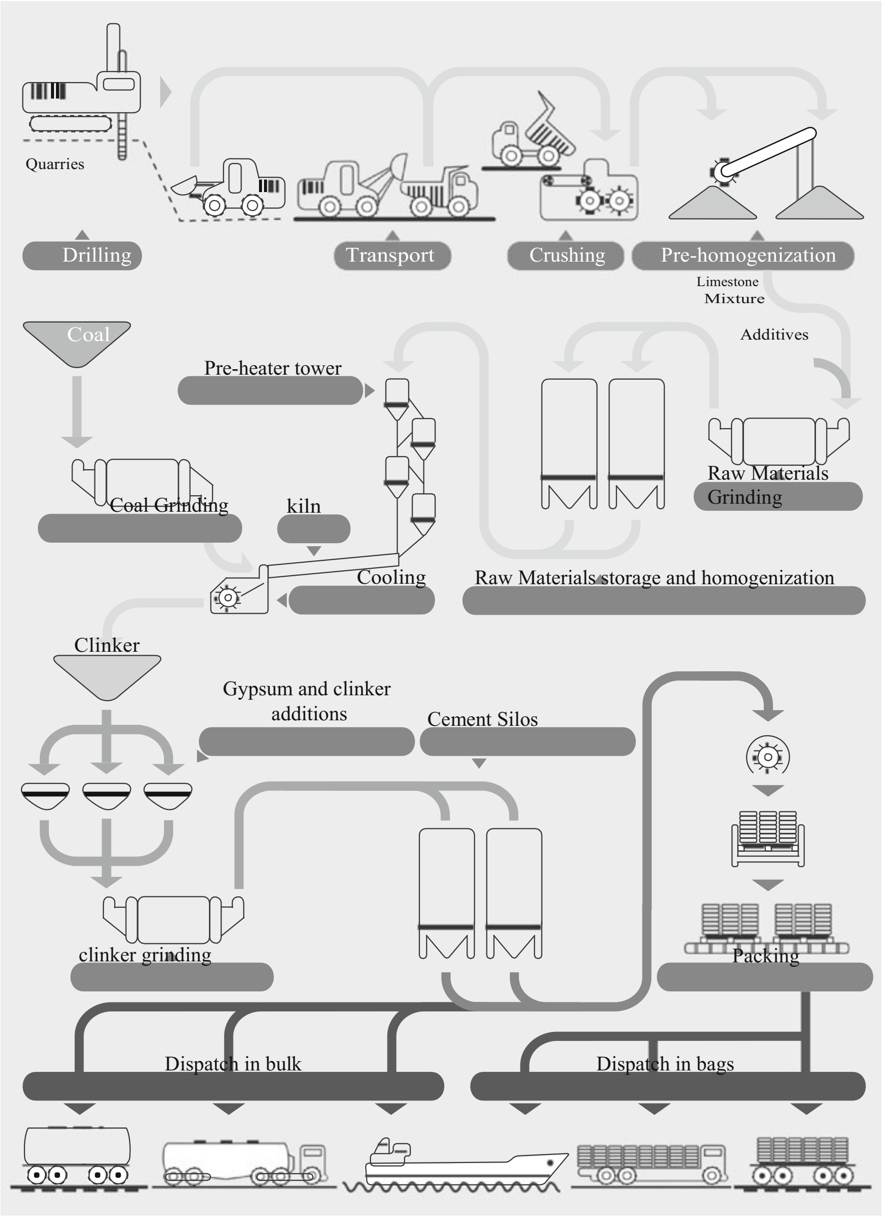

Fig. 1.4 Diagram of dry process of cement manufacturing

- Quality control of raw materials

  To minimize the variation in cement quality its manufacturing process requires a rigorous and effective control of raw materials processing, proportioning, and characterization—namely, in terms of chemical composition and particle size distribution. As such, raw materials quality checks are, typically, carried out at regular predetermined intervals of time that can be of 1, 2, or 4 h in different sampling points: both before and after the raw mill and after the raw meal silo.

  Currently, most of cement plants has at-line and online technologically advanced control systems equipped with automatic sampling systems, real-time chemical analyzers, and the ability to access to specific software, from remote locations, that automatically determines the necessary corrections. Clinker production is also strictly controlled—namely, the temperature profile in the preheater, kiln, and cooler.

To produce Portland cement clinker the chemical composition of the kiln feedstock must respect the relations, between the main oxides present in raw materials, shown in Table 1.6.

The Lime *Saturation Factor* (LSF) is a theoretical relationship that quantifies the lime content available in raw material to combine with the silica and alumina. Therefore, the control of this ratio value is important to ensure the absence of "free CaO." Theoretically, when the value of LSF is equal to 1, the total CaO react, and when it is higher than 1 there is an excess in the lime content that will persist in the final product in the form of "free CaO" (*see below* "clinker production").

The *Silica Ratio* (SR) is an empirical relationship that governs the silicates phases in the clinker. The SR value is inversely proportional to the amount of liquid formed in the kiln because only the alumina and ferric phases melt. Therefore, the higher the value of this ratio, the lower is liquid content in the kiln and, thus, the occurrence of chemical reactions is more difficult (*see below* "Production of Cement Clinker").

The *Alumina Ratio* (*AR*) determines: (1) the proportion of alumina to ferric phase in the clinker, which affect the properties of the final product (2) the temperature at which the liquid is formed in the kiln.

Production of Cement Clinker

- Chemical-mineralogical transformations in the preheater and the kiln

  The transformation of raw material's constituents into the clinker's constituents comprises a complex set of interdependent, simultaneous or successive, chemico-

Table 1.6 Relations between the main oxides present in raw materials to produce Portland cement clinker [2]

Designation	Ratio[a]	Values
Lime saturation factor (LSF)	$\frac{CaO}{2.80\ SiO_2+1.18\ Al_2O_3+0.65\ Fe_2O_3}$	0.92–0.98
Silica ratio (SR)	$\frac{SiO_2}{Al_2O_3+Fe_2O_3}$	2–3
Alumina ratio (AF)	$\frac{Al_2O_3}{Fe_2O_3}$	1–4

[a] Chemical formulas denote the corresponding oxide mass percentage

mineralogical transformations. These transformations which mechanisms are not yet totally clarified [2, 5, 23, 24] occur, essentially, in two of the plant's equipments: preheater tower and kiln, as represented in Fig. 1.5.

The raw meal enters at the top of the preheater tower (which is set of cyclones) [5, 25] and falls in counterflow with the hot gases coming from the kiln. During this process, the heat is transferred efficiently from the hot gases to the raw meal leading to the occurrence, mainly, of dehydration and decomposition of the clay and the decarbonation of about 40 % of the limestone ($CaCO_3 \rightarrow CaO + CO_2$).

Thereafter, the raw meal enters into a large cylindrical kiln whose diameter and length are about 5 and 80 m, respectively. The kiln is installed with an inclination from 2.5 to 5 % and is animated with a rotation speed of 1.5–2.5 r.p.m. to facilitate the slightly move of the material from the entrance towards the heated output end.

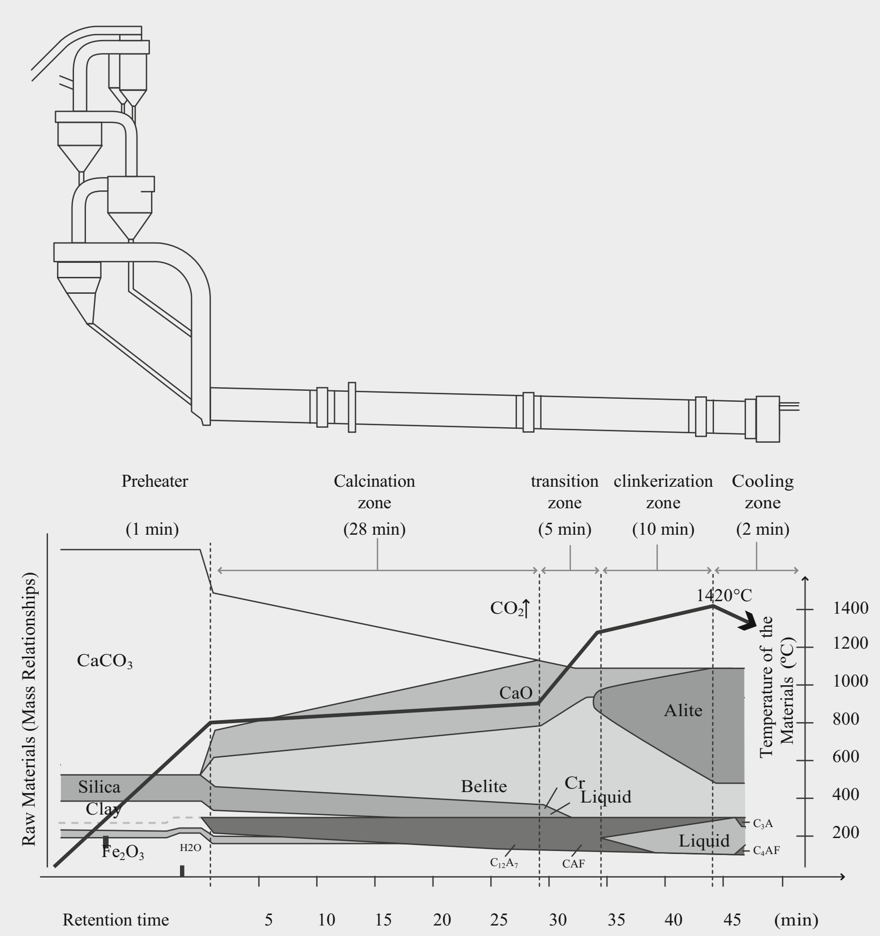

Fig. 1.5 Schematic representation of phase transformations occurring in the preheater and kiln during clinker production

Figure 1.5 shows that at the kiln entrance the material's temperature is typically between 700 and 800 °C. Throughout more than half the length of the kiln—*calcination zone*—occurs the decarbonation of limestone. Since this reaction is strongly endothermic, the temperature does not increase significantly. Simultaneously, begin the formation of belite ($C + S \rightarrow C_2S$), of calcium aluminate ($C + A \rightarrow C_{12}A_7$) and of calcium aluminoferrite ($C + A + F \rightarrow C_2(A,F)$) from the reaction of the newly formed CaO with the other phases of silica, alumina, and ferrite.

When the decomposition of limestone is completed, the following kiln zone called *transition zone* begins, in which at around 5 min and at about 10 % of kiln's length, the temperature of the materials increases rapidly from 900 to 1,250 °C. In this zone, there is a significant additional formation of belite and the aluminate phases, which were formed earlier, begin to originate tricalcium aluminate (C_3A) and tetracalcium aluminoferrate (C_4AF).

Thereafter, the materials proceed to the hottest kiln zone called *clinkerization zone*, where, at the approximated temperature of 1,330 °C, the aluminate, ferrite, and part of belite phases melt [23, 24]. Thus, henceforward the chemical reactions take place in a semisolid state that facilitates the atomic diffusion and reaction between the elements, providing the necessary conditions to the formation of alite, mainly from the reaction of the belite with residual CaO ($C_2S + C \rightarrow C_3S$). This compound is mainly responsible for the high mechanical strength of modern cements.

The highest temperature reached in the kiln is approximately 1,420 °C (Fig. 1.5) at about 4/5 of the kiln's end [26]. The material that emerges from this zone is called *clinker* and is, mainly, composed of various phases of which the most important are alite, belite, and aluminate and ferrite. Theoretically, the reaction of C_3S formation consumes all the CaO still available in the kiln. However, approximately 0.5–1 % of CaO always remain uncombined and is, often, referred to as "free CaO" or "free lime."

- Cooling of clinker

  The thermal history of clinker cooling—which occurs in the kiln's *cooling zone*—has a significant influence on its mineralogical composition and is important to achieve the best strength-giving properties of the final product. As such, it is essential, that the clinker is cooled down very quickly [24, 27], mainly at the beginning (occurring a decrease from the clinkering temperature to about 1,350 °C in 1 s) in order to:

  – Preserve, in a metastable state, the more reactive polymorphic forms of the C_3S and β-C_2S (these compounds are only thermodynamically stable at temperatures above 670 °C and 1,275 °C, respectively).
  – Ensure that there is no significant transport of material between clinker phases, i.e., that the different phases crystallize with little mutual interference.
  – Promote nucleation of more crystals (instead of crystals growth) that facilitates the subsequent grinding phase.

  The clinker of common cements emerging from the kiln is rounded nodules having a typical diameter up to 40 mm (Fig. 1.6).

Fig. 1.6 Clinker at kiln exit

Table 1.7 Crystal size of tricalcium and dicalcium silicate clinker phases, which typically are individualized [27]

	Crystals	
Phase	Size (μm)	Morphology
C_3S	25–65	Hexagonal
C_2S	20–40	Rounded

- Composition and microstructure of clinker

  As previously referred, clinker is composed essentially by the following phases: C_3S—30–70 %; C_2S—10–30 %; C_3A—5–10 %, and C_4AF—5–15 % (values represents the percentages, by mass, of their typical occurrence). The standard EN 197-1:2000 specifies that Portland cement clinker shall consist of at least two-thirds, by mass, of calcium silicates (C_3S and C_2S), the mass ratio C/S shall not be less than 2 and that the content of magnesium oxide (M) shall not exceed 5 %, by mass.

  Typically, clinker particles larger than 3–5 μm are polymineral [28], consisting of silicate crystals—which size and morphology are described in Table 1.7—surrounded by an interstitial matrix consisting of aluminate and ferrite phases. Nature, size, and morphology of crystals formed are determined by the composition of raw materials and the manufacturing process conditions. Figure 1.7 shows an image of a clinker particle cross-section obtained by optical microscopy.

  The potential mineralogical composition of a Portland cement clinker can be estimated from the results of its chemical composition analysis [2, 29] using Bogue's equations, shown in Table 1.8. However, it should be kept in mind that these relations were established based on $CaO–SiO_2–Al_2O_3–Fe_2O_3$ phase diagram at clinkerization temperature, considering two assumptions which are unlikely to occur:

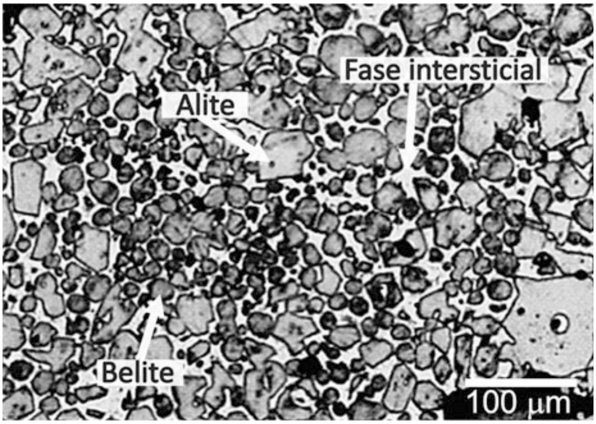

Fig. 1.7 Cross-section image of a clinker particle obtained by optical microscopy

Table 1.8 Bogue's equations (chemical formulas represent the mass percentages of the oxides)

Phase	Oxides content (obtained by chemical analysis)
C_4AF	$=3.043\ (Fe_2O_3)$
C_3A	$=2.650\ (Al_2O_3) - 1.692\ (Fe_2O_3)$
β-C_2S	$=-3.071\ (CaO) + 8.602\ (SiO_2) + 5.068\ (Al_2O_3) + 1.0785\ (Fe_2O_3)$ or
	$=2.8675\ (SiO_2) - 0.7544\ (C_3S)$
C_3S	$=4.071\ (CaO) - 7.602\ (SiO_2) - 6.718\ (Al_2O_3) - 1.430\ (Fe_2O_3)$

- Chemical equilibrium between crystallized phases is maintained during and after the cooling of the clinker.
- The main phases of clinker are pure, i.e., no alterations in phase diagram are considered due to the presence of interstitial or substitutional ions in the crystal structures of clinker phases.

Despite the mineralogical composition estimated by the Bogue's equations is not absolutely accurate (typically underestimating C_3S content and overestimating C_2S content), the calculations are so easy to perform that these relations are still commonly used in industry [2]. However, nowadays, most cement plants are equipped with the experimental X-ray diffraction technique, to perform a quantitative analysis of clinker phases automatically and in real time.

As referred above, the compounds that constitute the clinker are not as simple as the chemical formulas written above might indicate. In fact, they are not pure, often containing other elements in their crystal lattices. In addition, free oxides may also exist, for example, CaO and MgO. The minor constituents present in the clinker can: (1) be originated from the raw materials, (2) be introduced during the manufacturing process, particularly from fuel or from the refractory lining inside the kiln, or (3) be deliberately added. Although their content, in general, does not exceed 1 % by mass [2, 23, 30], these compounds influence the

Fig. 1.8 Gypsum at clinker mill inlet

production process and chemico-mineralogical composition of the clinker, and therefore affect the properties of the final product.

- Final grinding of clinker with gypsum

  Cement is the product obtained by intergrinding the clinker with 3–8 % by mass of gypsum ($CaSO_4 \cdot 2H_2O$ or $C\overline{S}H_2$). Figure 1.8 shows a typical photo of the gypsum at the clinker grinding mill inlet. In most cement plants, the final grinding of the clinker/gypsum blends are carried out in ball mills consisting of a tube rotating about a horizontal axis and that uses steel balls as grinding media [31].

  Gypsum is added to the cement as set regulator, since it:

  - Slows down C_3A hydration, preventing the occurrence of "quick" (flash) set of cement (Sect. 1.4.1.2).
  - Accelerates calcium silicates hydration leading to an increase in the compressive strength development, mainly, during the early ages [2].

  However, excess of calcium sulfate added to the cement is likely to promote dimensional instability in the hardened cement, due the formation of expansive hydrated compounds, such as ettringite ($C_6A\overline{S}_3H_{32}$).

  The increase of the specific surface area of the cement particles, i.e., the increase of fineness, accelerates the hydration rate and therefore, accelerates strength development, mainly at early ages. As such, the final grinding is a major factor influencing the class of strength of the cement. Figure 1.9 shows a photo of Portland cement type CEM I 52.5 R, at the clinker mill exit.

  The specific surface area (SSA) of cement particles of the ordinary early strength Portland cements (as defined in standard EN 197-1) ranges from 300 to 340 m^2/kg, whereas SSA of cement particles of high early strength cements ranges from 400 to 550 m^2/kg [29]. For cements with additions content lower than 20 % by mass, 90 % of cement particles should be finer than 90 μm

Fig. 1.9 Portland cement type CEM I 52,5R

[23]. When the content of additions is higher than 20 %, 90–95 % of the particles should be finer than 45 μm [30].

The other main constituents, beside clinker, considered in standard EN 197-1 for common cements—namely, blast furnace slag, silica fume, pozzolan, fly ash, shale, and limestone—may be added to the cement at this final grinding step (Sect. 1.4.2).

1.4.1.2 Hydration

The mixture of cement with water initiates a series of chemical hydration reactions. These reactions occur at different rates and mutually influence each other, leading to chemical, physical, and mechanical changes of the system. The hydrated compounds bind to each other, giving adhesive and cohesive properties to cement. At the macroscopic scale, the hydration process leads to the conversion of the water-cement system into a solid matrix. This matrix is microscopically uneven and porous and serves as a binder in cement-based materials. The cement hydration mechanism is complex and is, still, not fully understood.

The hydration reactions of cement constituents—C_3S, C_2S, C_3A, and C_4AF and $C\overline{S}$—are exothermic [32]. Figure 1.10 shows a scheme of the typical evolution of heat released as a function of hydration time.

It is commonly accepted to divide the scheme shown in Fig. 1.10 into five distinct areas and associate each of them with a distinct period (stages) of the hydration mechanism of a polymineralic cement particle. These periods (phases) are described below [2] and schematically represented in Fig. 1.11:

Pre-induction—In the first few minutes after mixing cement with water, there is a short period of fast reactions. In this period, mainly C_3A and C_4AF react with water and $C\overline{S}$ leading to the formation of a layer of an amorphous gel, rich in

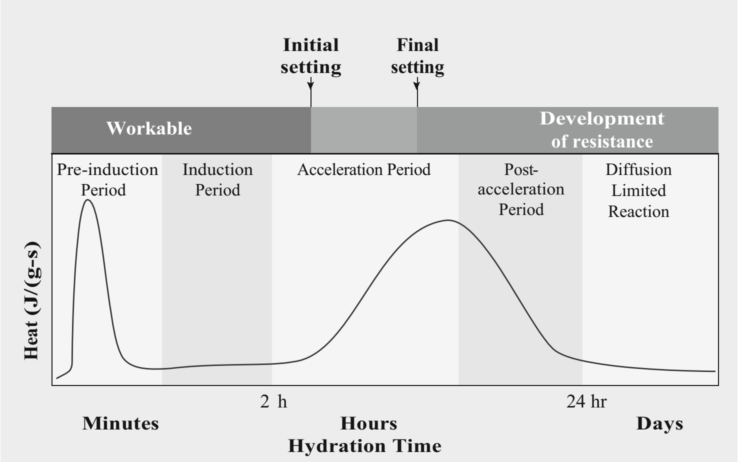

Fig. 1.10 Schematic heat evolution as a function of cement hydration time (and correspondence with the periods (or stages) of the cement hydration mechanism)

alumina, around the cement particles. Short rods of ettringite (AFt) are also detectable. This reaction is responsible for the initial significant amount of heat released.

Induction (*or dormant*) *period*—Chemical reactions occur in a small scale originating a negligible heat released.

Acceleration (*or post-induction*) *period*—there is a reacceleration of hydration reactions and heat release which reaches a maximum at a time that is usually less than 12 h after the initial mixing. This behavior is mainly due to the hydration reactions of calcium silicates, namely C_3S forming a layer of C-S-H gel around the cement particles, which are commonly called "outer C-S-H." These reactions induce a lost of plasticity in the cement paste that becomes a non-deformable rigid material (without, however, significant strength) in a process called setting. At the end of this period, about 30 % of the cement has hydrated, and the cement paste has undergone both initial and final setting.

Post-acceleration period—there occurs a gradual decrease in hydration reaction rate leading to a progressive decrease of heat release. The hydration of calcium silicates continues with a progressive increased contribution of the hydration of β-C_2S. The C-S-H gel begins to deposit inside of the hydration shell formed in the previous hydration periods and is called "Inner C-S-H." After about 18 h of cement hydration, a secondary hydration reaction of the aluminates (C_3A and C_4AF) restarts, forming additional AFt crystals which are markedly more acicular than those formed earlier. Sometimes, this process has associated a significant heat released.

Diffusion-limited reaction period—After 1–3 days of cement hydration, reactions significantly slow down owing to the diffusional limitation of compounds in the solid state. "Inner C-S-H" continues to form and a new aluminate phase appears,

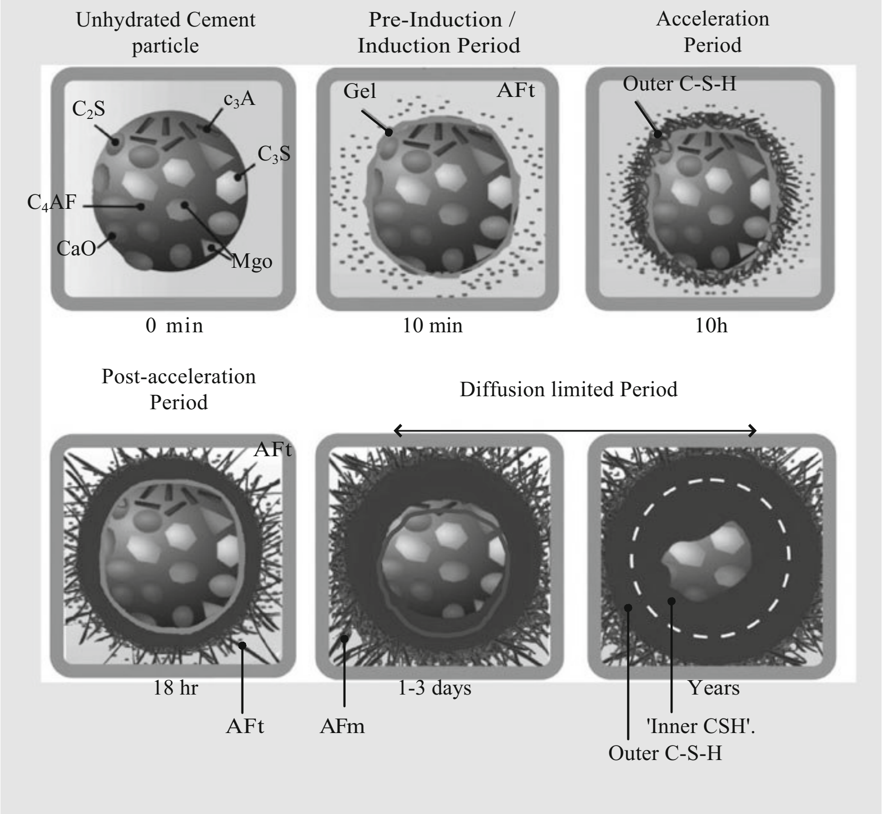

Fig. 1.11 Scheme of the different periods (or stages) of the hydration mechanism of a polymineral cement particle: *C_3S* tricalcium silicate, *C_2S* dicalcium silicate, *C_3A* tricalcium aluminate, *C_4AF* tetracalcium aluminoferrite, *C-S-H* calcium silicate hydrate, *AFt* calcium trisulfoaluminate hydrated, *AFm* calcium *mono*sulfoaluminate hydrated

the calcium *mono*sulfoaluminate hydrated (AFm). Hydration of cement proceeds throughout years, essentially forming additional "inner C-S-H" from β-C_2S.

Table 1.9 shows the hydration reactions of clinker main constituents, assuming that they are pure.

Calcium silicates hydrated (C-S-H), formed from the hydration of C_3S and C_2S, constitute 50–60 % of the solid phases present in hardened Portland cement pastes. They are the primarily responsible for the binding properties and high mechanical resistance developed by these materials.

When C_3A comes into contact with water tends to hydrate rapidly, forming C_3AH_6 and causing a "quick" (flash) setting that gives rise to a material with low mechanical strength. Moreover, the premature material's stiffening makes difficult

Table 1.9 Hydration reactions of clinker main constituents

Compound		Reaction
C_3S		$C_3S + (3 + y - x)\,H \rightarrow C_xSHy + (3 - x)\,\underset{\text{(portlandite)}}{CH}$
C_2S		$C_2S + (2 + y - x)\,H \rightarrow C_xSHy + (2 - x)\,\underset{\text{(portlandite)}}{CH}$
C_3A	Without gypsum	$2C_3A + 21H \rightarrow C_4AH_{13} + C_2AH_8 \rightarrow 2C_3AH_6 + 9H$
	With gypsum	$C_3A + 3C\overline{S}H_2 + 26H \rightarrow \underset{\text{(ettringite)}}{C_6A\overline{S}_3H_{32}} \rightarrow \underset{\text{(AFm)}}{3C_4A\overline{S}H_{12}}$
C_4AF		$C_4AF + 3C\overline{S}H_2 + xH \rightarrow \underset{\text{(AFt)}}{C_6(A,F)\,\overline{S}_3H_{32}} \rightarrow \underset{\text{(AFm)}}{3C_4(A,F)\overline{S}H_{12}}$

Note: Calcium silicates hydrated have a variable chemical composition, CxSHy. In the domain of the cement chemistry, these compounds adopted the abbreviated notation C-S-H (Table 1.5)

the hydration of the other cement constituents to proceed. As such, gypsum, $C\overline{S}H_2$, is added to control C_3A hydration (Sect. 1.4.1.1). In the presence of gypsum, the hydration of C_3A forms ettringite (Table 1.9) that act as a protective barrier against the continuation of the C_3A hydration and that allow the hydration of other cement constituents. Gypsum is, therefore, a regulator set that is always added to the common cements.

Both, the hydration of C_3A and C_4AF ends up forming a calcium mono sulfoaluminate hydrated, *AFm*, more stable than *AFt* phases such as ettringite (Table 1.9).

1.4.1.3 Correlation Microstructure–Properties

The microstructure of the cement-based materials is essentially determined by the compounds formed during the hydration reactions of the clinker's constituents (Table 1.9). The mechanism of cement hydration, whose periods (stages) have been previously described (Sect. 1.4.1.2) depends on different factors, such as: (1) type of cement used, in terms of its chemico-mineralogical composition and fineness, (2) water/cement ratio, (3) mixing procedure, (4) environmental conditions; (5) nature, number, and size of aggregates or other additives.

Figures 1.12 and 1.13 show images obtained by scanning electron microscopy (SEM) of the microstructure of hydrated cement pastes. The image shown in Fig. 1.12 was obtained by SEM in the secondary electron mode (SE) from a fracture surface of a hardened cement pastes. SEM-SE imaging of cement pastes provides images with low contrast. As such, observations have to be made in the inner surface of the pores and cavities, where products were able to freely crystallize [33]. Figure 1.12a shows acicular AFt crystals dispersed in a fibrous matrix of C-S-H. Figure 1.12b, and Fig. 1.12(c) show AFt crystals and dendritic (plate-like snow) crystals, corresponding to the typical crystallization morphology of CH. As expected, cement pastes with higher hydration time show more numerous as well as longer and thicker acicular AFt crystals (compare Fig. 1.12a with b and c).

In the images obtained by SEM in the backscattering electron mode (BSE), from polished flat surfaces, the contrast is mainly due to the differences in the chemical composition of the phases present in the hydrated cement pastes. Chemical

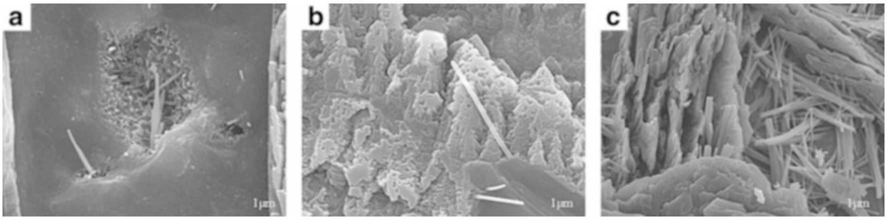

Fig. 1.12 Images of the microstructure of Portland cement pastes obtained by scanning electron microscopy in secondary electron mode (JEOL JSM-7001-F) from a fracture surface. (**a**) *At 2 days of hydration*: acicular crystals of calcium sulfoaluminates hydrated (AFt) dispersed in a fibrous matrix of calcium silicates hydrated (C-S-H); (**b**, **c**) *at 28 days of hydration*: acicular AFt crystals and crystals showing the dendritic typical crystallization morphology of calcium hydroxide (CH)

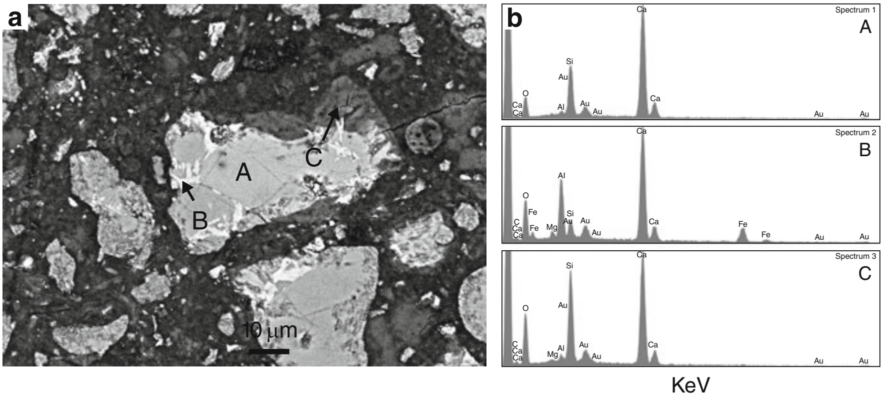

Fig. 1.13 Image of the microstructure of a Portland cement paste (at 28 days of hydration) obtained by scanning electron microscopy in backscattered electron mode from a flat-polished surface and corresponding energy-dispersive X-ray spectra (Jeol JSM-7001-F). *Note*: Peaks were standardized to the calcium peak high and the intensity has arbitrary units

elements with higher electron density (heavier atoms) give rise to higher brightness. Thus, SEM-BSE images can be used to detect contrasts between areas with different chemical composition providing relevant information on the chemical composition, namely if associated with local chemical analysis using energy-dispersive X-ray spectroscopy (EDX).

Moreover, the analysis of flat-polished surfaces also provides information on spatial distribution of solid phases and pores, as well as their interrelation mode in the internal structure, in a wide range of magnifications (~20–100,000×). Therefore, SEM-BSE imaging is effective to study the microstructure of cement-based materials [33, 34].

Figure 1.13 shows an SEM-BSE image of the microstructure of a hardened cement paste, as well as EDX spectra of some local chemical analysis. Since the unhydrated compounds have an average atomic number higher than the hydrated compounds, they exhibit higher brightness. Consequently, since there are still unhydrated compounds in the inner core (region A) of cement particles, this area exhibits higher contrast than the layer of hydrated compounds around the cement particles (region C). The calcium aluminoferrite phase, (spectrum B in Fig. 1.13b) exhibits the highest contrast due to the presence of iron in its composition (the atom of iron is heavier than most of the atoms present in cement pastes).

Hardened cement pastes have a complex microstructural organization, with local variations in terms of chemical composition, size, morphology, and crystallinity of the solid phases. In fact, the microstructure of these materials is even more complex than described, due to the presence of minor constituents that interfere with hydration mechanisms. Moreover, the microstructure is dynamic, changing over the lifetime of the material, as a result of physical processes and chemical reactions with both endogenous and exogenous compounds.

In brief, the phase composition of the hardened cement pastes is as follows (in which the values between brackets correspond to the estimated volume percentages of the phases present in a 14-month-old saturated paste prepared with a typical Portland cement hydrated at a water to cement ratio of 0.5.) [2, 28, 32]:

- *Solid phases*, namely products of the hydration reactions, C-S-H (48.7 %), CH (13.9 %), AFm (11.1 %), and AFt (3.6 %) and unreacted cement particles (2.6 %).
- *Pores* (16.0 %), with variable size, shape, and connectivity as well as unevenly distributed.
- *Water*, inside the pores network or bonded to the hydration products

Macroscopic scale properties, such as compressive strength, dimensional stability, and durability, are determined by the microstructure. Table 1.10 shows a brief description of the microstructure–property relationships of cement-based materials. These relationships are not still fully understood and quantified. However, evidence of its relevance originated their current intense scientific scrutiny by teams of civil, chemical, and materials engineers.

1.4.1.4 Chemical Degradation Reactions

Deterioration of cement-based materials is due to the occurrence of chemical and physical processes leading to changes in the microstructure and, therefore, in the properties and durability. Table 1.11 systematizes the main chemical degradation reactions of cement-based materials. These chemical reactions occur either between the constituent phases or between these constituents and other substances, endogenous or exogenous. The physical degradation processes—such as overloading, thermal gradients, impact, freeze thaw cycles, erosion, and abrasion—are out of the scope of this chapter.

Table 1.10 Relationships between the microstructure and properties of cement-based materials [2, 32, 81]

Constituent	Compressive strength	Dimensional stability	Durability
C-S-H	• Mainly responsible for mechanical strength due to van der Waals interactions which ensure the cohesion and adhesion between the solid phases	• In the hardened cement paste, it induces shrinkage, and creep by establishing additional van der Waals interactions (after water removal from the micropores)	• Its final intrinsic porosity affects the diffusion both of endogenous and exogenous substances and, therefore, influencing the occurrence of deleterious reactions
CH	• This compound fills the pores, contributing to the reduction of porosity and, hence, to increase the strength • On the other hand, its microstructure presents well-defined cleavage planes that may contribute to the decrease of the mechanical strength	• Compound dimensionally stable that restricts the volumetric changes associated with C-S-H	• Decreases the diffusion of endogenous and exogenous substances by filling the pores • Leaches out over time in the presence of water, increasing the porosity • Participates in alkali-silica reactions (ASR), carbonation, and reacts with acids
AFt and AFm	• Fills pores contributing to the reduction for porosity and, hence, to increase strength	The swelling associated with AFt phases contributes to expansion	• Participates in chemical reactions associated with sulfates attack
Porosity	• Determining factor for the mechanical strength: strength decreases with increasing porosity	• Particularly, small pores associated with the C-S-H gel phase plays a critical role in shrinkage and creep (due to water lost from this pores system)	• Affects the diffusion of both endogenous and exogenous substances and, therefore, influencing the occurrence of deleterious reactions
Water	• By increasing the water/cement ratio in the preparation of the material increases the porosity of the hardened material, and thus, decreases its strength	• The water removal from the pore system associated with the C-S-H gel phase induces shrinkage (due to the formation of van der Waals interactions)	• High water to cement ratio results in higher porosity and, therefore, higher permeability which, negatively affects durability

Table 1.11 Main chemical degradation reactions of cement-based materials [2, 82, 83]

Process		Mechanism	Source
Alkali-silica reactions (ASR)		The ASR is a deleterious reaction between the alkalis contained in cement with some potentially silica-reactive aggregates. Hydroxyl ions, OH^-, (present in the hydrated cement) break the Si–O–Si bonds of the aggregate to form anionic silicates (SiO^-). The negative charge of these anionic silicates is balanced by the positively charged alkali ions (Na^+, K^+) The product of this reaction, in the presence of water, are alkali-silica-hydrate swelling gels: $S + 2NaH/KH + H \rightarrow 2Na/K\text{-}S\text{-}H$ These swelling gels may create internal stresses leading to cracking and loss of cohesion, and thus, reducing the mechanical strength Controlling the ASR occurrence requires the use of cements with low alkali content—Na_2O equivalent[a] <0.6 % by mass and the use of unreactive aggregates	• *Alkali*: Na^+, K^+ • *Silica*: reactive aggregates
Sulfates Attack	Ettringite formation	Sulfate, mainly monosulfate, reacts with the aluminate phase of cement leading to expansive ettringite formation. The swelling associated to this product may create internal stresses leading to cracking and loss of cohesion: $C_4A\overline{S}H_{12} + 2Ca^{2+} + 2SO_4{}^{2-} + 20H \rightarrow C_6A\overline{S}_3H_{32}$ The extent of reaction is limited by the available aluminate phase content. Ca^{2+} is provided by the CH (a product of cement hydration). When it runs out, occurs decalcification of C-S-H and, the consequent material strength loss	• *External*. e.g., natural or residual water; soil; atmospheric SO_2, bacteria action • *Internal*. e.g., aggregates contamination; excess gypsum added
	Delayed ettringite formation (DEF)	DEF is a special case of internal attack by sulfates, which occurs when the material was subjected to high temperatures (>70 °C) leading to the destruction of the ettringite formed during cement hydration (Table 1.9). The presence of sulfates leads again to the formation of ettringite. Possible causes of heating are: (1) heat released during the cement hydration reactions, (2) curing at elevated temperatures, and (3) temperature rise in service (e.g., fire). This form of degradation can take years to become visible	
	Thaumasite formation	Thaumasite ($C_3S\overline{S}\overline{C}H_{15}$) is a product of the following reaction: $SO_4{}^{2-} + CO_3{}^{2-} + Ca^{2+} + H \rightarrow C_3S\overline{S}\overline{C}H_{15}$ This reaction requires high relative humidity and temperature between 5 and 10 °C [2]. The kinetics of thaumasite formation is fast, but does not occur frequently. Ca^{2+} ions arise from CH and C-S-H decomposition and may completely destroy the binding capacity of the cement paste, which becomes a friable material	Presence of: • Soluble sulfates • Carbonates, e.g., atmospheric CO_2, limestone

Carbonation	Consists in the formation of $CaCO_3$ ($C\overline{C}$) from the reaction of CO_2 with CH or with C-S-H. These reactions densify the cement paste matrix and, therefore, initially contribute favorably to its mechanical properties and to increase chemical resistance. However, when carbonation is extensive, the destruction of C-S-H (forming hydrated silica) induces a significant loss in the material strength. This reaction rate is faster in polluted environments. The most negative effects of carbonation, even when reaction extent is low, are: (1) pH reduction of cement paste matrix and (2) chloride ions (Cl^-) facilitated diffusion. Both factors increase vulnerability of the reinforcing steel to corrosion	• Atmospheric CO_2 • Relative humidity 50–70 %
Acid attack	CH formed during the hydration of cement (Table 1.9) is responsible for the high pH of ≈13 in cement pastes. Therefore, it is available to react to acids (HX) through the following reaction: $2HX + CH \rightarrow CaX_2 + H$ (wherein X is a negative acid ion) The nature of the salt formed (CaX_2), particularly with regard to its solubility, determines the resulting level of degradation. Low soluble salts block the pores, hinder the diffusion of substances and thus, make the acid attack reaction to proceed slower. This form of attack is particularly relevant when the CH content is low. In this case, acids react with the calcium arising from C-S-H decomposition. The most negative effect of acid attack is the decrease of the environment's pH leaving the eventual metal reinforcements vulnerable to corrosion	• Natural or polluted water, soils, polluted atmosphere, acid rain, etc.

[a] Na_2O equivalent corresponds to the total sodium and potassium oxides content expressed as equivalent sodium oxide, Na_2O equivalent $= Na_2O + 0.66\ K_2O$

1.4.2 Blended Cements

Blended cements are hydraulic binders in which cementitious materials (Sect. 1.4.2.1) or minerals (Sect. 1.4.2.2): (1) partially replace the clinker in the cement manufacturing process or (2) are added during the grout, mortar, or concrete preparation as partial substitutes for cement or fine aggregate.

In the cases that:

- The cementitious materials are *blast furnace slag*, *silica fume*, *pozzolan*, *fly ash*, or *burnt shale*, or else the mineral is *limestone*
- These additions meet the requirements and criteria set out in EN 197-1:2000 and EN 197-1:2000/A3: 2008 [20, 35], they can be interground with the clinker and gypsum in the clinker mill (Sect. 1.4.1.1) producing, common cements of types CEM II, III, IV, and V (Sect. 1.4). As such, the additions are considered main constituents of the cement. Figure 1.14 shows a picture of some of these additions at the clinker mill inlet.

1.4.2.1 Blended Cements with Cementitious Materials

Cementitious materials are compounds that participate in the hydration reactions by forming additional hydrated binder phases of calcium silicates hydrate (C-S-H) or calcium aluminosilicate hydrate (C-A-S-H) [2, 36–39]. These phases contribute for cement matrices densification and thus, to improve the mechanical properties and durability.

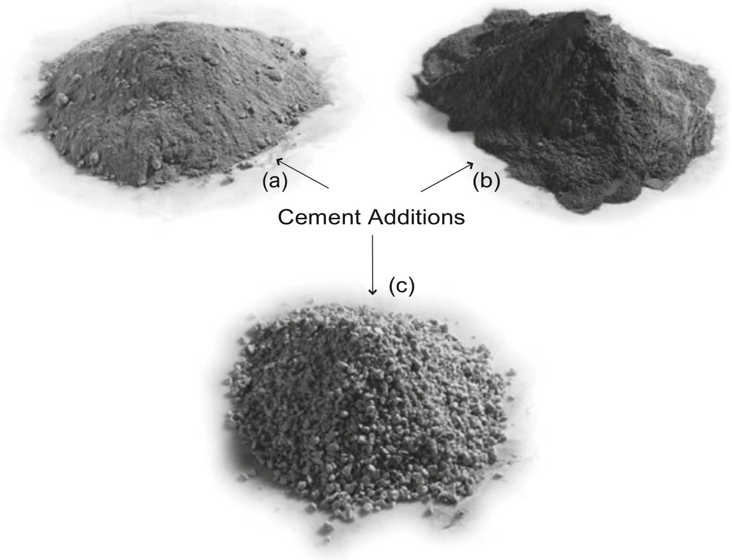

Fig. 1.14 Additions of common cements (**a**) pozzolan from the São Miguel Island in Azores, (**b**) fly ash, and (**c**) limestone

Table 1.12 Pozzolanic reactions of cementitious materials

Compound	Reaction
Siliceous	S + CH + H → C-S-H
Aluminosilicate[a]	AxSy + CH + H → C-A-S-H

[a]These compounds exhibit variable chemical composition, AxSy

Cementitious materials can be classified as [2]:

- *Pozzolans or pozzolanic materials*—siliceous or aluminosilicate compounds that react with water and calcium hydroxide (CH) to form calcium silicates hydrate (C-S-H) or calcium aluminosilicates hydrate (C-A-S-H) (Table 1.12). CH used in this reaction can be the product of the hydration reaction of calcium silicates present in the cement (Table 1.9). Pozzolans may come either from the nature (natural pozzolan) or from artificial sources such as the industrial by-products fly ash and silica fume.
- *Latent hydraulic binders*—calcium aluminosilicates that harden spontaneously through slowly reaction with water. Therefore, for the hardening process become significant requires the presence of an alkaline activator. This compound breaks the chemical bonds in the binder's amorphous (or glassy) phase and promotes the dissolution of ionic species and the formation of C-A-S-H phases. Granulated blast furnace slag is an example of a latent hydraulic binder.

Latent hydraulic binders have chemical compositions broadly intermediate between those of pozzolans and Portland cement, as schematically represented in the diagram phases $CaO–SiO_2–Al_2O_3$ (Fig. 1.1). Table 1.13 lists typical chemical composition and physical properties of selected cementitious materials.

Cementitious materials are also referred to in literature as *supplementary cementitious materials* (SCM) or *mineral additions*. However, the term "mineral additions," although commonly used in the context of cementitious materials, is not rigorous because to exhibit pozzolanic activity these materials have to be essentially in amorphous state and minerals are typically crystalline compounds.

Partial replacement of clinker or cement with cementitious materials has the following potential advantages:

- Environmental: Reduce the CO_2 emissions and fuel consumption associated with the process of clinker manufacture. When cementitious materials are industrial by-products, they also concur to mitigate the amount of quarried natural resources as well as the dust, noise, and vibration associated with the raw material preparation for clinker manufacture. In concomitance, the reuse of by-products reduces the amount of waste disposed of to landfills.
- Economic: (1) reduce the cement manufacturing cost, and (2) in the case of using an industrial by-product there is an increase in profits by adding value to a waste.
- Technological: (1) mechanical properties improvement due to the additional formation of C-S-H or C-A-S-H phases that contribute to the cement paste

Table 1.13 Typical chemical composition and physical properties of cementitious materials [43]

	Natural pozzolan	Artificial pozzolans			Latent hydraulic
	S. Miguel Island, Azores[a]	Silica fume	Fly ash		Granulated blast furnace slag
			Siliceous	Calcareous	
SiO_2 (% by mass)	60	90	52	35	35
Al_2O_3 (% by mass)	18.2	0.4	23	18	12
Fe_2O_3 (% by mass)	4.3	0.4	11	6	1
CaO (% by mass)	1.4	1.6	5	21	40
SO_3 (% by mass)	0	0.4	0.8	4.1	9
Na_2O (% by mass)	4.7	0.5	1.0	5.8	0.3
K_2O (% by mass)	5.1	2.2	2.0	0.7	0.4
Specific surface area (m^2/kg)	~6,000[b]	20,000	420	420	400
Density	0.8	2.54	2.65	2.65	2.94

[a] Cimentaçor—Cimentos dos Açores, Lda

[b] Highly variable in the natural state. The table presents the SSA value with which it is incorporated in cement

matrix densification, (2) decrease of rate and total amount of heat released because the hydration reaction of cementitious materials is less exothermic than that of cement, (3) durability improvement, since the densification of the cement/pozzolans blended paste matrix hinders the diffusion of both endogenous and exogenous substances reducing the likelihood of deleterious reaction occurring. In addition, the partial replacement of clinker with cementitious materials that, typically, have low alkali content or that have the ability to trap alkali ions reduce the risk of alkali-silica reactions. Moreover, the consumption of CH in the pozzolanic reactions reduces the availability of the reagents required for the formation of $C_6A\overline{S}_3H_{32}$ (Table 1.11) and thus, mitigates sulfates attack.

Although, cementitious materials incorporation, typically, is favorable to the hydraulic binder's properties, the effect of each material depends on: (1) reactivity—determined by the chemical and mineralogical composition; (2) particles size—in terms of fineness level, particle size distribution, and specific surface area; (3) clinker composition and fineness; (4) water to cement ratio of cement paste; and (5) the presence of other constituents and additives.

Next follows a brief description of cementitious materials with greater commercial and technological importance. Table 1.14 systematizes the main effects of incorporating these materials on the properties and durability of blended cements properties.

- Natural pozzolans

  The use of hydraulic binders containing natural pozzolans to improve their mechanical properties became widespread in the Roman Empire, based on

Table 1.14 Blended cements containing silica fume, fly ash, and blast furnace slag: comparison of blended cement-based materials properties in relation to those of plain cement pastes

Cementitious Materials	Compressive strength	Durability	Others	References
Silica fume	• Increases the strength (*often used as a constituent of high strength cement*)	• Decreases the diffusion of endogenous and exogenous substances and thus the likelihood of deleterious reactions	• Decreases the heat generated by hydration reactions	[2, 5, 28, 37, 38, 83]
		• Increases the resistance against ASR and sulfates attack	• Improves the workability of the pastes in the fresh state (due to the spherical morphology of the particles)	
			• Accelerates the hydration of alite (and thus, accelerates the setting time)	
			• Decreases the bleeding	
			• Densifies the interfacial transition zone between cement paste and aggregate	
Fly ash	• Decreases the strength at 2 and 28 days	• Decreases the diffusion of endogenous and exogenous substances	• Decreases the heat generated by hydration reactions and delays the time of peak temperature	[23, 28, 38, 43]
	• Achieve similar long-term strength than that of plain cement	• Increases resistance against ASR	• Worsens the workability of fresh pastes	
Blast furnace slag	• Decreases hydration reaction rate: decreases early-time strength	• Decreases the diffusion of endogenous and exogenous substances	• Decreases the heat generated by hydration reactions and delays the time of peak temperature (*often used when low heat of hydration important requirement*)	[2, 5, 39, 40, 43]
	• Achieve similar strength than that of plain cement at 28 days	• Increases resistance against ASR and to attacks by sulfates and acids (*often used as sulfate-resistant cements*)		
	• Achieve higher strength than that of plain cement (at a cement replacement level >50 %)			

empirical knowledge (Sect. 1.2). Currently, it is known that heating these compounds at temperatures between 400 and 900 °C (calcination) causes dehydration and the destruction of its crystal structure. In this process, natural pozzolans are converted into amorphous phase materials in order to increase their pozzolanic reactivity [2, 40]. The *optimal activation* temperature is dependent on the actual pozzolan chemico-mineralogical composition. Above a certain temperature value, the compounds adopt a crystalline structure, and the pozzolanic reactivity decreases again.

Pozzolans include a wide variety of materials with different chemical compositions, mineralogical nature, and geological origins; therefore, their classification is not consensual [38]. In some literature, for example, the thermally activated natural pozzolans are considered artificial. This was not the criteria followed in the Standard EN 197-1:2000 [20] and that was adopted in this chapter. Table 1.13 shows typical chemical composition and physical properties of natural pozzolans that meet the requirements of the standard EN 197-1:2000 [20].

Typically, the use of natural pozzolans in blended cements leads to the technological and environmental advantages described in Sect. 1.4.2.1. However, the high diversity in pozzolans composition determines the need to evaluate the actual effect of each pozzolan on the properties and the durability of the blended cements.

The draft of the European standard EN 197-1:2009 [41]—resulting from the review of the standard EN 197-1:2000, currently underway—considers that some common cements of type CEM IV (Annex I) containing natural pozzolan classified, as sulfate-resisting common cement.

- Silica fume

  Silica fume is an industrial byproduct of the production of silicon metals and ferrosilicon alloys. This small spherical particles consisting of amorphous silica is obtained from the condensation of vapors produced during the melting process of high-purity quartz to silicon, at elevated temperatures. Table 1.13 shows the typical chemical composition and physical properties of silica fume.

  Silica fume is a very reactive pozzolanic material, mainly, due to the high specific surface area of its particles. In addition, these particles fill the intergranular void between cement particles (*filler* effect) and thus densify and homogenize the cement paste microstructure [42]. Table 1.14 systematizes the main effects of silica fume incorporation on the properties of cementitious materials.

  Silica fume is also referred to in literature as *microsilica* or *condensed silica fume* (although this term often refers to extremely pure synthetic silica).

- Fly ashes

  Fly ashes are industrial byproducts collected in the dedusting unit after combustion coal in electric power plants. Fly ashes cover a large family of powders which composition is basically located in the ternary CaO–SiO_2–Al_2O_3 system (Fig. 1.1) although they can have a wide range of chemico-mineralogical compositions depending on to the source and properties of the coal burned. Table 1.13 shows their typical chemical composition and physical properties.

According with standard EN 197-1:2000 [20], fly ashes are categorized as: siliceous (V) and calcareous (W). The main difference between these classes is their content in calcium oxide. Siliceous fly ashes contain less than 10 % of calcium oxide and are pozzolanic materials. Calcareous fly ashes contain more than 10 % of calcium oxide, and therefore is often referred to as "high calcium" fly ash. Class W fly ashes have enough calcium to be a latent hydraulic binder, i.e., only needs water to hydrate and harden [5, 43]. The effects of incorporating fly ashes on cement-based materials properties depend on their exact composition, content, and size and shape of their particles; however, their most common effects on the cement pastes are systematized in Table 1.14.

The draft of a European standard EN 197-1:2009 [41]—resulting from the review of the standard EN 197-1:2000, currently underway—considers that some common cements of type CEM II (Annex I) containing class V fly ashes may be classified as sulfate-resisting common cements.

- Blast furnace slag

Blast furnace slag is an industrial by-product generated in the manufactures of pig iron from iron ore. This slag is obtained in liquid state, at high temperatures, in the lower part of the blast furnace. The chemical composition of this slag is basically located in the ternary $CaO–SiO_2–Al_2O_3$ system (Fig. 1.1) and its mineralogical composition is determined by the cooling rate [2, 40, 44]. If the molten slag is fast-cooled tends to mainly form amorphous calcium aluminosilicates which are latent hydraulic binders. Slow cooling rate leads to a polycrystalline solid with no cementitious properties. In this case, the slag can be incorporated in cement-based materials as fine aggregate [5].

The hydraulic reactive slags are also referred to in literature as *granulated blast furnace slag* (GGBFS or GGBS), or *high-slag blast furnace*. In this chapter, the term *slag* will also be used as a synonym.

To comply with the European standard EN 197-1:2000 requirements, slag shall contain at least two-thirds, by mass, of the sum of CaO, MgO, and SiO_2 with the ratio $(CaO + MgO)/SiO_2$ greater than 1.0. The remainder contains Al_2O_3 together with small amounts of other oxides. Table 1.13 shows the typical chemical composition and physical properties of the slag.

In general, the hydraulic reactivity of these compounds increases with: (1) amorphous phase content, (2) alkali content, mainly CaO, and (3) particles fineness. Latent hydraulic properties of the slag can be promoted by the following alkaline activators: $Ca(OH)_2$, clinker, Portland cement, NaOH, KOH, Na_2CO_3, and Na_2SiO_3 [40]. All these compounds break the chemical bonds of the amorphous phases, causing the dissolution of ionic species and the subsequent formation of C-A-S-H phases.

$C\overline{S}$ is also an effective activator, in high alkaline environments, acting as a Ca^{2+} source and leading to significant amount of ettringite ($C_6A\overline{S}_3H_{32}$) formation. Table 1.14 describes the most frequent effects of the slag as partial replacement of Portland cement clinker.

> The draft of the European standard EN 197-1:2009 [41]—resulting from the review of the standard EN 197-1:2000, currently underway—considers that some common cements type CEM III containing slag (Annex I) might be classified as sulfate-resisting low early strength common cements.

1.4.2.2 Blended Cements with Limestone

Blended cements may contain mineral additions—both from natural and artificial sources—neither with pozzolanic nor latent hydraulic properties (Sect. 1.4.2.1). Thus, strictly speaking, mineral additions are not cementitious materials, although they are often referred to as such in literature. High-purity limestone is an example of such additions (Fig. 1.14).

When a limestone—that fulfills the requirements laid down in the standard EN 197-1:2000 [20]—is interground with the clinker and gypsum in the clinker mill (Sect. 1.4.1.1), it is produced Portland-limestone cement type CEM II (Annex I). The consumption of this type of cement has been steadily increased in Europe in the last decades and, currently is the most widely used (Fig. 1.3).

Mineral additions are often referred to as “fillers” in a reference to its physical effects, in terms of: (1) complete the granulometric curve of the fine aggregates, and (2) fill the pores in hardened state of the cement-based materials.

Traditionally, *fillers* were considered chemically inert. However, it is currently accepted that they can participate in chemical reactions to a limited extent. Namely, fillers react in particular with C_3A, forming various carboaluminate phases—$C_4A\overline{C}H_{11}$ as well as accelerate the hydration rate of the clinker constituent C_3S, probably due to the multiplied nucleation sites [2, 43, 45].

The effects of limestone on cement-based materials properties depend on its chemical composition as well as on the particles size distribution. Table 1.15 systematizes the most frequent effects of partial clinker replacement with this mineral.

1.5 Other Hydraulic Binders’ Families

In addition to the family of common cements as specified in standard EN 197-1:2000 (Sect. 1.4), there are other hydraulic binders’ families which include hydraulic limes and other special cements. These cements have distinct or additional properties than those of common cements and were designed to address specific technological, environmental, economic, and aesthetic needs. Some of these special cements are already commercially available, although on a small scale, satisfying particular market niches [40].

The following sections describe other families of hydraulic binders that have been selected on the base of traditional widespread use in certain market sectors, namely hydraulic lime (Sect. 1.5.1) as well as other binders that have been reported as promising alternatives to common cements (Sects. 1.5.2–1.5.4).

Table 1.15 Blended cements containing limestone: comparison of blended cement-based materials properties in relation to those of plain cement pastes

Addition	Compressive strength	Durability	Others	References
Limestone	• Effect on early age strength depends on particle size dimensions (PSD): greater fineness ⇒ increase strength	• Contributes to increase porosity. However, in optimized limestone cement, the diffusion of endogenous and exogenous substances is equivalent to that of plain cement	• Increases cement's hydration rate	[40, 45]
	• Optimized limestone cement achieve similar long-term strength than that of plain cement	• Typically increases resistance to attack by sulfates, because the consumption of C_3A decreases ettringite formation	• Increases the heat generated by hydration reactions and accelerates the time of peak	
		However, there is a higher potential risk of thaumasite formation	• Setting time regulator: can partially replace gypsum	
			• Decreases the water bleeding	

1.5.1 Hydraulic Limes

Chronologically, the first family of hydraulic binders identified and used as such was the hydraulic lime (Sect. 1.2). These binders are obtained by calcining (thermal activation between 1,000 and 1,250 °C) limestone with a significant clay content (between 6.5 and 20 %, by mass) [4, 46]. Clay may be present, in enough amount, in the earthy or impure argillaceous limestone or has to be added to the limestone.

The thermal activation process occurs in a lime kiln comprising the following steps:

- Clay decomposition ($Al_2O_3{\cdot}SiO_2 \rightarrow Al_2O_3 + SiO_2$).
- Limestone decarbonation ($CaCO_3 \rightarrow CaO + CO_2$).
- Reaction of CaO with SiO_2 and Al_2O_3, forming calcium silicates and aluminates. The main hydraulic phase formed Phase is C_2S. A significant amount of CaO (above 3 %) does not react, remaining under the name of "free CaO". Small amounts of other phases are also formed, such as C_3A, C_2AS, C_3S, and C_4AF [23, 46].

Hydraulic limes set and harden due to the hydration reactions of these compounds. Therefore, the hydraulic properties depend on the composition of the hydraulic phases which were determined by clay content in raw material as well as by temperature profile and permanence time in the lime kiln.

The hydration reaction of the free CaO (quicklime) to $Ca(OH)_2$ (quenched or slaked lime) on kiln lime exit leads to material's expansion, since $Ca(OH)_2$ density is, sensibly, half of that of CaO. Therefore, sufficient water should be provided at kiln exit to hydrate the available quicklime but not to cause calcium silicates and aluminates phases hydration and set at this stage. This slaking step in hydraulic lime manufacture has two advantages: (1) the mechanical effect of expansion contributes to increase the fineness of the final product, facilitating the subsequent grinding process and (2) prevents harmful subsequent expansions. In the subsequent milling step, gypsum is usually added to regulate the setting (Sect. 1.4.1.1).

Setting and hardening of hydraulic lime occur in two stages. Initially, the process is predominantly hydraulic, i.e., associated to the hydration reactions of the calcium silicates and aluminates, that occur when mixed with water and/or under water. These reactions are for conceptually similar to those presented in Table 1.9 and lead to the formation of C-S-H phases, C-A-H, and AFm. Subsequently, the recarbonation, i.e., the reaction of the slaked lime with atmospheric carbon dioxide ($Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$) is also part of the hardening process [4, 47].

European standard EN 459-1:2002 [48] specifies the composition, the requirements (mechanical, physical, chemical, and durability), and conformity criteria that hydraulic limes and their constituents must meet to be certified for civil engineering applications. Typically, lime hydraulic mortars exhibit: (1) lower mechanical strength, reduced shrinkage, increased workability, and longer time period between the initial and final set than common cement-based mortars and (2) good adhesion to cement substrates.

Hydraulic lime has a wide range of applications, namely: (1) as filler in bitumen pavements [49], (2) in soil properties improvement [50], (3) in renders, plaster, and masonry mortars both for new construction and rehabilitation [46].

1.5.2 Special Portland Cements

The term "special Portland cements" is adopted to identify families of hydraulic binders that, although not in compliance with the standard for common cements, EN 197-1:2000 (Sect. 1.4), are made with common cement clinker, or with a clinker which manufacturing process is basically the same. As such, the hydration processes of the "special Portland cements" are also similar to those of the common cements and their binding properties arise mainly from hydrated calcium silicates.

So far, the European Committee for Standardization (CEN) elaborated standards to define the composition, specifications, and conformity criteria for the following "special Portland cements": very low heat special cement, EN 14216:2005 [51]; masonry cement, EN 413-1:2006 [52]; and supersulfated cement, EN 15743:2010 [53].

Table 1.16 systematizes possible modifications in the common cements composition—in regard to the prescribed in the standard EN 197-1:2000—to produce "special Portland cements," as well as describe corresponding required alterations in the clinker manufacturing process and the effects on the properties of the final product (Sect. 1.4.1).

The current awareness that the reinforcement of sustainable construction is dependent on the ability to address economic and environmental issues in an integrated way have been promoting studies on the reuse of pozzolanic wastes (not considered in the standard EN 197-1:2000 [20]) as partial surrogates for cement clinker.

In this scope, the cementitious properties of several industrial wastes, such as rice husk ash, sugar cane straw [54, 55], paper sludge [56], and a waste from oil industry [57, 58] is being under scrutiny. The results of these studies show that, typically, these wastes exhibit the advantages of the other pozzolanic materials (Sect. 1.4.2.1).

As such, although the use of these wastes is not yet widespread, it might be anticipated that they will play a relevant role in the future of the hydraulic binder's industry (Sect. 1.1), in line with the progressively increasing use of blended common cement (types CEM II to V) in relation to plain Portland cement type CEM I (Fig. 1.3).

1.5.3 Aluminous Cements

The family of aluminous cements includes several hydraulic binders—whose main constituent is the monocalcium aluminate $CaO{\cdot}Al_2O_3$ (CA)—that have a chemistry completely different from that of the family of common cements. Cements of this family are also referred to as "high alumina cements," and "calcium aluminate cements" (CACs).

Aluminous cements were first patented by Jules Bied (French) in 1908, with the main objective of minimizing the problems associated with sulfates attack. Its industrial production began in 1918, in the French company Lafarge, under the trade name "Ciment Fondu Lafarge" [59]. Its current production is far below that of common cements, and it is considerably (eight to ten times) more expensive [5]. Their mostly used application is in precast, but they are also used as a refractory material and in specific constructions, in which common cements do not perform adequately.

The typical chemical composition of aluminous cements, expressed in mass percentages, is as follows: CaO, 36–42 %; Al_2O_3, 36–42 %; Fe_2O_3, 12–20 %; and Si_2O, 3–8 %. There may also exist other minor constituents such as Ti_2O <2 %, MgO $\leq$1 %, SO_3 <0.5 %, and alkalis <0.5 % [59]. In terms of mineralogical composition, their typical phases are: CA, 40–50 %; C_4AF, 20–40 %, and a combination of other minority crystalline phases including $C_{12}A_7$, CA_2, β-C_2S, C_2AS, FeO, TiO_2, and pleochroite $Ca_{20}Al_{32-x}Fe^{2+}{}_x\ Si_xO_{68}$ ($x \sim 2.5$–3.5) [60]. The

Table 1.16 Special Portland cements: differences in cements composition, in clinker manufacturing process and in the properties of the final product in relation to those of common Portland cements [40]

Composition		Production	Properties
High C_3S	$>C_3S$ content	• LSF[a] ≥ 1	• High initial strength
	$<C_2S$ content	• >Energy consumption	• High hydration heat
	$\geq C_3A$ content		• Fast heat release rate
High C_2S	$>C_2S$ content	• LSF[a] $= 0.8–0.9$	• Slow strength development
	$<C_3S$ content	• <Energy consumption and pollutant emissions	• Low hydration heat
		• Clinker easier to grind	• Slow heat release kinetics
High C_3A	$>C_3A$ content	• Silica ratio decreases	• Expansive cement
		• Alumina ratio increases	
Low C_3A	$<C_3A$ content	• Silica ratio decreases	• Resistant to sulfates attack[b]
			• Low hydration heat
Low iron content	Fe_2O_3 <0.5 % content	• Alumina ratio ≥ 10	• White cement
		• Clinkerization temperature increases	• <Setting time
			• Higher compression and strength resistance
			• Highly susceptible to sulfates attack
High iron content	$>Fe_2O_3$ content	• Alumina ratio decreases	• Very dark gray
		• Clinkerization temperature decreases	• Resistant to sulfates attack
Low alkali content	$Na_2O_{equivalent}$[c] <0.6 %	• Use of raw materials with low alkali content	• Increases the resistance against ASR
		• Partial removal of hot kiln gases (with significant alkalis content) that would ordinarily enter the preheater	• Increases free CaO content
			• Disfavor pozzolanic reactions

[a] Abbreviation of "Lime Saturation Factor" (Sect. 1.4.1.1)

[b] The draft of the European standard 197-1:2009 [41] considers that some cement clinkers type CEM II and CEM IV (containing siliceous fly ash and natural pozzolans, respectively Annex I) with limited maximum C_3A content are sulfate-resisting common cements

[c] $Na_2O_{equivalent} = Na_2O + 0.66\ K_2O$, i.e., total sodium and potassium oxides content expressed as equivalent of sodium oxide

content of the minority individual phases is less than 10 % [2]. Figure 1.1 shows the composition of these cements in the ternary CaO–SiO_2–Al_2O_3 diagram of phases.

When an aluminous cement is mixed with water occur strongly exothermic chemical reactions giving rise to hydrated compounds, mainly calcium aluminates hydrates (C-A-H) and insoluble alumina trihydrate (AH_3). These compounds convert the suspension water/cement into a solid matrix through a hardening process similar to that of the other hydraulic binders.

The hydration process of these cements, at room temperature, has an initial induction (dormant) period lasting 2–3 h during which the reactions proceed to a small extent. After this, the hydration reactions become very fast with two consequences: a huge amount of heat release and a fast strength development with the final strength being reached within 1 or 2 days (at higher temperatures, this period can be still significantly shortened). This high amount of heat released in a short period of time limits their application in some engineering works, where the heat dissipation is more difficult, e.g., in massive structures construction [40].

The products of the hydration reactions of the main aluminous cements constituents, CA and other calcium aluminates, are temperature dependent [5, 59]. As such,

- Below 10 °C: the product is essentially, CAH_{10}.
- Between 10 and 25 °C: the products are C_2AH_8 and AH_3.
- Above 25 °C: the products are C_3AH_6 and AH_3.

CAH_{10} and C_2AH_8 phases are metastable, thus, with time, they inevitably and irreversibly convert themselves in C_3AH_6, which is the only calcium aluminous hydrated phase thermodynamically stable. The kinetics of conversion of these reactions (Table 1.17) is also highly temperature dependent: the extent of the reactions may not be significant for days or years at temperatures below 40 °C and at higher temperatures they occur in few hours [40, 59].

The conversion process of the metastable phases into the stable hydrated phase (Table 1.17) is associated to a decrease in the solid volume of the hydrated compounds. This reduction is, typically, around 10–12 % [59] and, as a consequence, the porosity increases and the strength of the aluminous cement may significantly decrease with time. An effective way to mitigate the inconvenience of this chemical shrinkage is to prepare the aluminous cement pastes with insufficient water/cement ratio, i.e., less than 0.4 [59] (the typical water/cement ratio needed to reach complete hydration is 0.7) to avoid the full hydration of calcium aluminates. As such, the water produced in conversion reactions (Table 1.17) will

Table 1.17 Conversion reactions of metastable phases, CAH_{10} and C_2AH_8, initially formed in the hydration process of aluminous cement into the thermodynamically stable phase, C_3AH_6

Reactions
$3CAH_{10} \rightarrow C_3AH_6 + 2AH_3 + 18H$
$3C_2AH_8 \rightarrow 2C_3AH_6 + AH_3 + 9H$

react with the still anhydrous cement, forming additional amount of metastable phases. These compounds are less dense than stable products increasing the solid volume and, therefore, preserving the dimensional stability and low porosity of the hardened material [59].

One type of cement belonging to this family—the CAC—is standardized in the European Union by the standard EN 14647:2005+ AC: 2006 [61] which specifies its composition, requirements (mechanical, physical, chemical, and durability), and conformity criteria. This standard also includes a guide for the correct use of CAC in concrete and mortar.

The properties of the aluminous cements that make them particularly attractive for some applications in civil engineering are:

- *High initial strengths*: the fast hydration rate of calcium aluminates phases leads to high early strength gains. These cements can achieve a compressive strength of 20–40 MPa within 24 h. This is the reason for its large application in pre-casting.
- *Strength development at low temperatures*: the fast heat released during these cements hydration promotes self-heating that supports the progress of the hydration, at low temperatures. Therefore, at temperatures down to −10 °C, these cements exhibit normal setting followed by fast strength gains.
- *Resistance at high temperature* (*refractory materials*): The binding C-A-H phase maintains its stability at high temperatures, up to around 110 °C (on the contrary to the hydration products of common cements). As such, aluminous cements are extensively used as refractory materials.
- *Resistance to aggressive environments* (acid, sulfates, maritime environment as well as natural water with high content of dissolved CO_2): the most important feature determining the high resistance of these materials in aggressive environment is related to cement matrix compactness. However, to achieve this such compactness requires, as previous mentioned, pastes being prepared with water/cement ratio lower than 0.4, in order to minimize the increase porosity and, thus, permeability, of material over time, inherent to the conversion reactions shown in Table 1.17.

In addition, the resistance of these cements in aggressive environments is also due to: (1) the absence of CH and ettringite which contribute to the high resistance to sulfates attack [40, 59], (2) the binding C-A-H phases are stable in a wide range of acidic solutions until pH ~4 for $\mathrm{pH} < 7$, whereas the main hydration products of common cements, C-H-S and C-H, are quickly decomposed for $\mathrm{pH} < 7$, (3) thickness of the carbonation layer (Sect. 1.4.1.4) is typically thin because the calcium carboaluminate hydrates formed during the reaction of the binding C-A-H phases with CO_2 also contribute to the densification of the paste matrix making the reaction more difficult to proceed.

1.5.4 Calcium Sulfoaluminate Cements

Calcium sulfoaluminate cements (shorthand, CSA cements, or $C\overline{S}AC$) constitute another family of hydraulic binders which binding ability arises from the formation of ettringite— $C_6A\overline{S}_3H_{32}$ —instead of from C-S-H as with the common cements (Sect. 1.4). These cements were mainly developed in China in the 1970s aiming to develop self-stressed concrete pipes making use of the expansive properties of ettringite. The current production of CSA cements is expressive: one million tons per year [62]. Cements of this family are also referred to as "sulfoaluminate cements."

The main advantage of this cement family is the lower environmental impact of its manufacturing process since it: (1) emits less amount of CO_2; (2) consumes less fuel (due to the clinkerization at lower temperatures and to the easier-to-grind clinker) (3) may use various industrial by-products as raw material such as phosphogypsum, fly ash, blast furnace slag, and red mud.

CSA cements technological benefits mainly rely on the possibility of some taylormade properties for particular applications—namely, the initial strength and the dimensional stability. In fact, these cements can be either expansive or have a controlled shrinkage.

CSA cement clinker is prepared by heating a mixture of limestone, bauxite (or aluminous clay), and gypsum at 1,300–1,350 °C [62]. The result is a friable easy-to-grind clinker whose composition is included in the $CaO–Al_2O_3–SiO_2–Fe_2O_3–SO_3$ system. The major phases present are: C_2S, C_4AF, $C_4A_3\overline{S}$ (also called yeelimite), and $C\overline{S}H_2$ (gypsum) [40, 63]. These cements may also have other minority phases in their constitution, such as C_4AF, $C_{12}A_7$, $C_2A\overline{S}$, and $C\overline{S}$. Table 1.18 shows a comparison of these cements typical compositions with those of common Portland cements (Sect. 1.4.1).

When the CSA cements is mixed with water, their constituents hydrate and convert the water/cement suspension into a solid matrix through a hardening process conceptually similar to those of the other cements.

The hydration of C_2S and C_4AF forms C-S-H and CH; the hydration of C_4AF forms $C_6(A,F)\overline{S}_3H_{32}$ and $C_4(A,F)\overline{S}H_{12}$ (as has been seen for Portland cement hydration, Table 1.9); and the hydration of $C_4A_3\overline{S}$ and $C\overline{S}H_2$ forms ettringite—$C_6A\overline{S}_3H_{32}$—which is, in the case of CSA cements, the main binding compound. However,

Table 1.18 Comparison of typical Portland compositions with sulfoaluminous cement [5]

	Cement	
Phase	CSA (%)	Portland (%)
C_3S	0	50–70
C_2S	10–60	10–30
C_3A	0	5–10
C_4AF	0–40	5–15
$C_4A_3\overline{S}$	10–90	0
$C\overline{S}H_2$	15–30	3–8

Table 1.19 Hydration reactions of the main calcium sulfoaluminate constituent, $C_4A_3\overline{S}$ depending on calcium hydroxide (CH) content

CH content	Reaction
CH (<24–25 % by mass)	$C_4A_3\,\overline{S} + 2C\overline{S}H_2 + 36H \rightarrow \underset{\text{(ettringite)}}{C_6A\overline{S}_3H_{32}} + 2AH_3$
CH (>24–25 % by mass)	$C_4A_3\,\overline{S} + 8C\overline{S}H_2 + 6CH + 74H \rightarrow \underset{\text{(ettringite)}}{3C_6A\overline{S}_3H_{32}}$

the hydration reaction mechanism and the microstructure of ettringite strongly depend on the presence of CH [2, 40, 62] as it is systematized in Table 1.19. In fact, if:

1. *CH content lower than 24–25 % (by mass)*: the hydration reaction rate is fast and the formed ettringite is dimensionally stable raising significantly the cements early strength (e.g., 15 MPa after 2 h of hydration [63] and 40 MPa after 6 h of hydration [64]).
2. *CH content higher than 24–25 % (by mass)*: the formed ettringite is low dense, exhibiting expansive behavior or with controlled shrinkage.

The production of cements with high early strength versus expansive cements can also be controlled by the following variables: (1) manufacturing conditions, (2) purity and relative amount of the main phases present, and (3) content and nature of minor phases.

The technological characteristics of CSA cements, which make them attractive for some applications in civil engineering are: (1) high early strength, particularly suitable for precast construction, (2) set and harden at low temperatures, (3) frost resistance, during the harden process and in service, (4) sulfates attack and salt water resistance [28]. However, these cements are very susceptible to carbonation [65], increasing the risk of corrosion (Sect. 1.4.1.4).

The use of expansive CSA cements is particularly important in water reservoirs and concrete water pipes because their self-stress contributes to minimize water leaking risk [2]. They are also recommended for use in repair systems because they strongly adhere to common cements (Sect. 1.4), even if carbonated [62].

1.5.5 Alkali-Activated Cements

Alkali-activated cements, or alkaline cements, constitute a family of hydraulic binders which binder's ability is due to hydrated aluminosilicate compounds—*geopolymers* or *inorganic polymers*—with the chemical formula:

$$\mathrm{M}n\left[(\mathrm{SiO_2})_z \cdot \mathrm{AlO_2}\right]_n \cdot w\mathrm{H_2O},$$

wherein M is a cation, usually Na^+, K^+, and Ca^{2+}; n, the polymerization degree; w, is the hydration degree; and z may assume the values 1, 2, or 3 [66]. Geopolymers have a chemical composition similar to that of zeolites,[6] but they have an essentially amorphous microstructure [66].

The setting and hardening processes of these binders result from an alkali activation of an aluminosilicate precursor by an alkali activator solution, typically at a temperature slightly higher than room temperature [67]. Theoretically, all aluminosilicates materials are potential precursors of these alkali-activated binders. The exact mechanism of the activation reaction is not still completely understood [68–71] but includes the dissolution of the precursor aluminosilicate producing a complex mixture of silicate, aluminate, and aluminosilicate species. These species, present in a supersatured solution, copolymerize to form the geopolymers which are amorphous to semicrystalline three-dimensional aluminosilicates.

Examples of precursors already scrutinized are either natural aluminosilicates such as kaolin [72] or industrial by-products including blast furnace slags [70, 73], fly ashes [67, 70], and tungsten mine waste [74].

The properties of geopolymers are determined by [67, 72, 75]:

- The chemico-mineralogical composition and fineness of aluminosilicate precursors. However, the relative importance of these parameters is not consensual. Typically, higher calcium content, higher amorphization degree and higher fineness degree of the precursor lead to geopolymers with improved binding properties. As such, in some cases a prior thermal treatment of the precursor is required in order to increase their amorphization degree.
- The composition and concentration of the alkali activator solution. The most used activators are sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium waterglass ($Na_2O \cdot nSiO_2$), potassium waterglass ($K_2O \cdot nSiO_2$) or a mixture of these compounds.
- The mixing procedure and curing conditions, the presence of other constituents (such as CaO or additives), the order in which the constituents are mixed and the curing temperature.

Often alkali-activated binders reveal technological advantages over ordinary Portland cements (Sect. 1.4) such as: (1) better both early age and long-term mechanical strength, (2) grater durability against attack by sulfates, acids, and bacteria; and (3) refractory properties [71, 75].

In addition, the use of these binders have environmental benefits because they have a much smaller environmental impact compared to common Portland cements in terms of non-renewable raw materials and energy consumption as well as in terms of CO_2 footprint. Moreover, if the aluminosilicate precursor is a waste from other industry, geopolymers production also diverts the wastes from being disposed of in landfills.

The interest on the alkali-activated cements family has been identified in the early 1940s of the last century [12, 68, 76]. However, the research activities focused

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[6] Zeolites are crystalline aluminosilicates which basic structural units are $[Si0_4]$ and $[AlO_4]^-$ tetrahedra bonded to each other by sharing of oxygen atoms. The negative electrical charges of $[AlO_4]^-$ tetrahedra are compensated by extraframework cations. Typically, these cations are derived from elements of the 1st or 2nd group of the Periodic Table.

on these binders only became significant after the 1980s mainly due to the Joseph Davidovit's research work that support the patent of a binder based on alkali-activated metakaolin [77]. Thenceforward, the number of studies on this subject has grown exponentially resulting in different commercial trademarks such as PYRAMENT®, PZ-Geopoly®, and Geopolycem® [77, 78].

Beyond the enormous potential that this binders family present, it is still necessary to increase the knowledge on these binders to make them economically viable for widespread use and to minimize their technological disadvantages (significant shrinkage, low workability, and high dependence on curing conditions, namely temperature) [12, 68].

1.6 Final Remarks

Construction is a vital sector since the beginning of the civilization that contributed over time to improve human well-being and social equity. Since hydraulic binders are constituents of the construction materials most commonly used, their properties and performance determine the constructive solutions adopted as well as economic and environmental impacts resulting from this industrial sector.

The awareness of the very high ecological footprint associated with the common cements manufacturing has been the main driving motivation towards the development of alternative binder systems with lower environmental impact. Moreover, the innovative binders shall comply with construction materials standards, performance targets, market needs as well as meet criteria of cost-benefit analysis.

Within this scope, it has been assessed the available opportunities to both improve the manufacturing process of the common cements and to change their chemical composition—namely, incorporating by-products from other industries (Sect. 1.5.2). Concomitantly, it has been under intense scientific scrutiny the viability of large-scale industrial use of other hydraulic binders based on a chemistry different from that of common cements (Sects. 1.5.3–1.5.5) [9, 12, 79, 80].

Hydraulic binders are grouped into families of materials depending on their chemistry. These families, in turn, include different binders, each of which is constituted by multiphase systems that are influenced by the preparation conditions, the environment, and the conditions in service. As such, the variety and complexity of the binders' systems required a systematization and synthesis during the writing of this chapter. The selection criteria adopted intended to present the more generalized use and the most promising materials. In this way, this chapter aimed to provide the fundamental knowledge to contribute to a better understanding of the hydraulic binders. This should help to correctly support the decisions to be made at the project design level as well as during the execution and maintenance of engineering works. It will also allow the monitoring of scientific and technological advances that lie ahead.

Annex I

Table A1.1 Designation, notation, and composition of the 27 products in the family of common cement as defined by the standard EN 197-1:2000

Main types	Notation of the 27 products (types of common cement)		Composition (percentage by mass)										
			Main constituents										Minor additional constituents
			Clinker	Blast furnace slag	Silica fume	Pozzolana		Fly ash		Burnt shale	Limestone		
						Natural	Natural calcined	Siliceous	Calcareous				
			K	S	D	P	Q	V	W	T	L	LL	
CEM I	Portland cement	CEM I	95–100	–	–	–	–	–	–	–	–	–	0–5
CEM II	Portland-slag cement	CEM II/A-S	80–94	6–20	–	–	–	–	–	–	–	–	0–5
		CEM II/B-S	65–79	21–35	–	–	–	–	–	–	–	–	0–5
	Portland-silica fume cement	CEM II/A-D	90–94	–	6–10	–	–	–	–	–	–	–	0–5
	Portland-pozzolana cement	CEM II/A-P	80–94	–	–	6–20	–	–	–	–	–	–	0–5
		CEM II/B-P	65–79	–	–	21–35	–	–	–	–	–	–	0–5
		CEM II/A-Q	80–94	–	–	–	6–20	–	–	–	–	–	0–5
		CEM II/B-Q	65–79	–	–	–	21–35	–	–	–	–	–	0–5
	Portland-fly ash cement	CEM II/A-V	80–94	–	–	–	–	6–20	–	–	–	–	0–5
		CEM II/B-V	65–79	–	–	–	–	21–35	–	–	–	–	0–5
		CEM II/A-W	80–94	–	–	–	–	–	6–20	–	–	–	0–5

(continued)

Table A1.1 (continued)

Main types	Notation of the 27 products (types of common cement)		Composition (percentage by mass)										Minor additional constituents
			Main constituents										
			Clinker	Blast furnace slag	Silica fume	Pozzolana		Fly ash		Burnt shale	Limestone		
						Natural	Natural calcined	Siliceous	Calcareous				
			K	S	D	P	Q	V	W	T	L	LL	
		CEM II/B-W	65–79	–	–	–	–	–	21–35	–	–	–	0–5
	Portland-burnt shale cement	CEM II/A-T	80–94	–	–	–	–	–	–	6–20	–	–	0–5
		CEM II/B-T	65–79	–	–	–	–	–	–	21–35	–	–	0–5
	Portland-limestone cement	CEM II/A-L	80–94	–	–	–	–	–	–	–	6–20	–	0–5
		CEM II/B-L	65–79	–	–	–	–	–	–	–	21–35	–	0–5
		CEM II/A-LL	80–94	–	–	–	–	–	–	–	–	6–20	0–5
		CEM II/B-LL	65–79	–	–	–	–	–	–	–	–	21–35	0–5
	Portland-composite cement	CEM II/A-M	80–94	6–20									0–5
		CEM II/B-M	65–79	21–35									0–5

CEM III	Blast furnace cement	CEM III/A	35–64	36–65	–	–	–	–	–	–	–	0–5
		CEM III/B	20–34	66–80	–	–	–	–	–	–	–	0–5
		CEM III/C	5–19	81–95	–	–	–	–	–	–	–	0–5
CEM IV	Pozzolanic cement	CEM IV/A	65–89	–	11–35					–	–	0–5
		CEM IV/B	45–64	–	36–65					–	–	0–5
CEM V	Composite cement	CEM V/A	40–64	18–30	–	18–30			–	–	–	0–5
		CEM V/B	20–38	31–50	–	31–50			–	–	–	0–5

Table A1.2 Mechanical and physical Requirements for the common of cements as defined in the standard EN 197-1:2000

Strength class	Comprehensive strength (MPa)				Initial setting time (min)	Soundness (expansion) (mm)
	Early strength		Standard strength			
	2 days	7 days	28 days			
32.5 N	–	≥16.0	≥32.5	≤52.5	≥75	≤10
32.5 R	≥10.0	–				
42.5 N	≥10.0	–	≥42.5	≤62.5	≥60	
42.5 R	≥20.0	–				
52.5 N	≥20.0	–	≥52.5	–	≥45	
52.5 R	≥30.0	–				

Table A1.3 Examples of identification of common cements according to standards EN 197-1:2000 and EN 197-1: 2000/A 1:2004

Example	Description
Portland cement EN 197-1 CEM I 52.5 R	Portland cement conforming to EN 197-1 of strength class 52.5 with a high early strength
Portland-limestone cement EN 197-1 CEM II/B-L 32.5N	Portland-limestone cement conforming to EN 197-1 containing between 65 and 79 % by mass of limestone with a TOC content not exceeding 0.50 % by mass (L) of strength class 32.5 and an ordinary early strength
Portland-composite cement EN 197-1 CEM II/A-M (S-V-L) 32.5 R	Portland-composite cement containing in total a quantity of granulated blast furnace slag (S), siliceous fly ash (V), and limestone (L) of between 6 and 20 % by mass and of strength class 32.5 with a high early strength
Blast furnace cement EN 197-1 CEM III/B 32.5N-LH	Blast furnace cement conforming to EN 197-1, containing between 66 and 80 % by mass of granulated blast furnace slag (S) of strength class 32.5 with an ordinary early strength and a low heat of hydration (LH) (*Note*: the heat of hydration of common cements defined as *low heat of hydration* should not exceed—according to EN 197-1:2000/A1:2004—the characteristic value of 270 J/g evaluated (1) at 7 days (according to the EN 196-8) or (2) at 41 h (according to EN 196-9))

References

1. Sousa Coutinho A (1988) Fabrico e Propriedades do Betão, vol II, 2nd edn. Laboratório Nacional de Engenharia Civil, Lisboa
2. Taylor HFW (1998) Cement chemistry, 2nd edn. Thomas Telford, London
3. Chatterjee AK (2004) Raw materials selection. In: Bhatty JI, Miller FM, Kosmatka SH (eds) Innovations in Portland cement manufacturing. Portland Cement Association, Skokie, pp 37–63

4. Coutinho JS (2006) Materiais de Construção—2. 1.^{a} Parte—Ligantes e Caldas. Departamento de Engenharia Civil, Faculdade de Engenharia da Universidade do Porto
5. Aïtcin P-C (2008) Binders for durable and sustainable concrete, 1st edn. Taylor & Francis, New York
6. Mertens G, Lindqvist J, Sommain D, Elsen J (2008) Calcareous hydraulic binders from a historical perspective. In: Historical mortars conference HMC 08, Lisbon, 24–26 September, pp 1–15. http://www.kuleuven.be/geology/mineralogy/Hydraulic%20binders.pdf
7. Oliveira GB (1999) A Indústria Portuguesa do Cimento, vol 1, 2nd edn. CIMPOR Cimentos de Portugal
8. International Cement Review (2009) Global cement report, 8th edn
9. Aïtcin P-C (2000) Cements of yesterday and today: concrete of tomorrow. Cem Concr Res 30 (9):1349–1359
10. Blezard RG (2000) Reflections on the history of the chemistry of cement. Society of Chemical Industry (SCI) Lecture Papers Series LPs, 104, pp 1–27
11. Varas MJ, Alvarez de Buergo M, Fort R (2005) Natural cement as the precursor of Portland cement: methodology for its identification. Cem Concr Res 35(11):2055–2065
12. Phair JW (2006) Green chemistry for sustainable cement production and use. Green Chem 8:763–780
13. Bispo C (2009) Marcação CE nos Cimentos, Seminário: Evolução da Marcação CE, Coimbra, Portugal. 1 de Abril. http://www.inform.pt/seminarios/emarcacaoce/pdf/atic_cb.pdf (May 2010)
14. Corish AT, Kerkhoff B (2004) European standards and specifications for cements. In: Bhatty JI, Miller FM, Kosmatka SH (eds) Innovations in Portland cement manufacturing. Portland Cement Association, Skokie, pp 1209–1218
15. Rasmussen JH (2007) Presentation of FLSmidth & Co. A/S, Carnegie Large Cap Seminar, 24 September. http://hugin.info/2106/r/1157431/223603.pdf (consulta em maio 2010)
16. Eurostat. http://epp.eurostat.ec.europa.eu/portal/page/portal/eurostat/home/ (February 2010)
17. US Census Bureau. International data Base. http://www.census.gov/ipc/www/idb/ (February 2010)
18. Worrell E, Price L, Martin N, Hendriks C, Meida LO (2001) Carbon dioxide emissions from the global cement industry. Annu Rev Energy Environ 26(1):303–329
19. Basheer PAM (2009) Concrete: an introduction. In: Forde EM (ed) Properties of hardened concrete. ICE manual of construction materials, vol 1. Thomas Telford, London, pp 57–60
20. EN 197-1:2000. Cement. Composition, specifications and conformity criteria for common cements
21. Miller FM (2004) Raw mix design considerations. In: Bhatty JI, Miller FM, Kosmatka SH (eds) Innovations in Portland cement manufacturing. Portland Cement Association, Skokie, pp 65–79
22. Chatterjee AK (2004) Materials preparation and raw milling. In: Bhatty JI, Miller FM, Kosmatka SH (eds) Innovations in Portland cement manufacturing. Portland Cement Association, Skokie, pp 81–136
23. Jackson PJ (1998) Portland cement: classification and manufacture. In: Hewlett PC (ed) Lea's chemistry of cement and concrete. Elsevier, Oxford, pp 25–94
24. Glasser FP (2004) Advances in cement clinkering. In: Bhatty JI, Miller FM, Kosmatka SH (eds) Innovations in Portland cement manufacturing. Portland Cement Association, Skokie, pp 331–368
25. Bech C, Mishulovich A (2004) Preheaters and precalciners. In: Bhatty JI, Miller FM, Kosmatka SH (eds) Innovations in Portland cement manufacturing. Portland Cement Association, Skokie, pp 269–286
26. Steuch HE (2004) Clinker coolers. In: Bhatty JI, Miller FM, Kosmatka SH (eds) Innovations in Portland cement manufacturing. Portland Cement Association, Skokie, pp 477–498

27. Campbell DH (1999) Microscopical examination and interpretation of portland cement and clinker, 2nd edn. Portland Cement Association, Skokie
28. Bye GC (1999) Portland cement. Composition, production and properties, 2nd edn. Thomas Telford, London
29. Lawrence CD (1998) The constitution and specification of Portland cements. In: Hewlett PC (ed) Lea's chemistry of cement and concrete. Elsevier, Oxford, pp 131–193
30. Tennis PD, Kosmatka SH (2004) Cement characteristics. In: Bhatty JI, Miller FM, Kosmatka SH (eds) Innovations in Portland cement manufacturing. Portland Cement Association, Skokie, pp 1069–1106
31. Strohman NR (2004) Finish milling and grinding. In: Bhatty JI, Miller FM, Kosmatka SH (eds) Innovations in Portland cement manufacturing. Portland Cement Association, Skokie, pp 499–517
32. Odler I (1998) Hydration, setting and hardening of Portland cement. In: Hewlett PC (ed) Lea's chemistry of cement and concrete. Elsevier, Oxford, pp 241–297
33. Costa C, Carvalho PA, Nogueira I (2009) Análise Microestrutural dos Materiais Cimentícios. Arte e Construção 229:38–41
34. Costa C, Carvalho PA (2009) O Pequeno Grande Mundo dos Cimentos. Arte e Construção 227:32–36
35. EN 197-1:2000/A3:2007. Cement. Composition, specifications and conformity criteria for common cements
36. Richardson IG (2008) The calcium silicate hydrates. Cem Concr Res 38(2):137–158
37. Diamond S, Sahu S, Thaulow N (2004) Reaction products of densified silica fume agglomerates in concrete. Cem Concr Res 34(9):1625–1632
38. Massazza F (1998) Pozzolana and Pozzolanic cements. In: Hewlett PC (ed) Lea's chemistry of cement and concrete. Elsevier, Oxford, pp 471–635
39. Morranville-Regourd M (2002) New cementitious systems and composite materials. In: Actas da seventh conference of the European Ceramic Society—ECerS-7, vol 3, Bruges, Belgium, pp 1841–1846
40. Odler I (2000) Special inorganic cements. Taylor & Francis, New York
41. DRAFT EN 197-1:2009. Cement. Composition, specifications and conformity criteria for common cements
42. Fidjestol P, Lewis R (1998) Microsilica as an addition. In: Hewlett PC (ed) Lea's chemistry of cement and concrete. Elsevier, Oxford, pp 679–710
43. Schmidt M, Middendorf B, Vellmer C, Geisenhanslueke C (2004) Blended cements. In: Bhatty JI, Miller FM, Kosmatka SH (eds) Innovations in Portland cement manufacturing. Portland Cement Association, Skokie, pp 1107–1148
44. Morranville-Regourd M (1998) Cements made from blastfurnace slag. In: Hewlett PC (ed) Lea's chemistry of cement and concrete. Elsevier, Oxford, pp 637–678
45. Hooton RD, Nokken M, Thomas MDA (2007) Portland-limestone cement: state-of-the-art report and gap analysis for CSA A 3000. Cement Association of Canada, SN3053, pp 1–59
46. Lanas J, Pérez Bernal JL, Bello MA, Alvarez Galindo JI (2004) Mechanical properties of natural hydraulic limestone-based mortars. Cem Concr Res 34(12):2191–2201
47. El-Turki A, Carter MA, Wilson MA, Ball RJ, Gc A (2009) A microbalance study of the effects of hydraulicity and sand grain size on carbonation of limestone and cement. Constr Build Mater 23(3):1423–1428
48. EN 459-1:2002. Building lime. Definitions, specifications and conformity criteria
49. Airey GD (2009) Bitumen properties and test methods. In: Forde EM (ed) ICE manual of construction materials, vol 1. Thomas Telford, London, pp 262–272
50. Agee A (2009) Right use of limestone in soil improvement, 1st edn. BiblioBazaar

51. EN 14216:2004. Cement. Composition, specifications and conformity criteria for very low heat special cements
52. EN 413-1:2004. Masonry cement. Composition, specifications and conformity criteria
53. Supersulfated cement. Composition, specifications and conformity criteria. Comité Europeu para a Normalização (TC-51)
54. Sousa Coutinho J (2003) The combined benefits of CPF and RHA in improving the durability of concrete structures. Cem Concr Compos 25(1):51–59
55. Frías M, Villar-Cociña E, Valencia-Morales E (2007) Characterisation of sugar cane straw waste as pozzolanic material for construction: calcining temperature and kinetic parameters. Waste Manag 27(4):533–538
56. García R, Vigil Villa R, Vegas I, Frías M, Sánchez de Rojas MI (2008) The pozzolanic properties of paper sludge waste. Constr Build Mater 22(7):1484–1490
57. Pacewska B, Bukowska M, Wilinska I, Swat M (2002) Modification of the properties of concrete by a new pozzolan—a waste catalyst from the catalytic process in a fluidized bed. Cem Concr Res 32(1):145–152
58. Costa C, Juenger M, Ferreira P, Carvalho PA (2009) Microstructural analysis of cement pastes blended with waste catalysts from oil refinery. In: European congress and exhibition on advanced materials and Processes EUROMAT 2009, 7–10 Set, Glasgow, UK
59. Scrivener KL, Capmas A (1998) Calcium aluminate cements. In: Hewlett PC (ed) Lea’s chemistry of cement and concrete. Elsevier, Oxford, pp 713–782
60. Sourie A, Glasser FP, Lachowski EE (1994) Microstructural studies on pleochroite. Br Ceram Trans 93(2):41–48
61. EN 14647:2005. Calcium aluminate cement. Composition, specifications and conformity criteria
62. Glasser FP, Zhang L (2001) High-performance cement matrices based on calcium sulfoaluminate-belite compositions. Cem Concr Res 31(12):1881–1886
63. Lawrence CD (1998) The production of low-energy cements. In: Hewlett PC (ed) Lea’s chemistry of cement and concrete. Elsevier, Oxford, pp 421–470
64. Péra J, Ambroise J (2004) New applications of calcium sulfoaluminate cement. Cem Concr Res 34(4):671–676
65. Quillin K (2001) Performance of belite-sulfoaluminate cements. Cem Concr Res 31(9): 1341–1349
66. Davidovits J (1991) Geopolymers. J Therm Anal Calorim 37(8):1633–1656
67. Diaz EI, Allouche EN, Eklund S (2010) Factors affecting the suitability of fly ash as source material for geopolymers. Fuel 89(5):992–996
68. Pacheco-Torgal F, Castro-Gomes J, Jalali S (2008) Alkali-activated binders: a review: part 1. Historical background, terminology, reaction mechanisms and hydration products. Constr Build Mater 22(7):1305–1314
69. Duxson P, Fernández-Jiménez A, Provis J, Lukey G, Palomo A, van Deventer J (2007) Geopolymer technology: the current state of the art. J Mater Sci 42(9):2917–2933
70. Oh JE, Monteiro PJM, Jun SS, Choi S, Clark SM (2010) The evolution of strength and crystal line phases for alkali-activated ground blastfurnace slag and fly ash-based geopolymers. Cem Concr Res 40(2):189–196
71. Xu H, van Deventer JSJ (2002) Geopolymerisation of multiple minerals. Miner Eng 15 (12):1131–1139
72. Pacheco-Torgal F, Castro-Gomes J, Jalali S (2008) Alkali-activated binders: a review. Part 2. About materials and binders manufacture. Constr Build Mater 22(7):1315–1322
73. Chen W, Brouwers H (2007) The hydration of slag, part 1: reaction models for alkali-activated slag. J Mater Sci 42(2):428–443
74. Pacheco-Torgal F, Castro-Gomes J, Jalali S (2009) Tungsten mine waste geopolymeric binder: preliminary hydration products investigations. Constr Build Mater 23(1):200–209
75. Xu H, van Deventer JSJ (2000) The geopolymerisation of alumino-silicate minerals. Int J Miner Process 59(3):247–266

76. Roy DM (1999) Alkali-activated cements opportunities and challenges. Cem Concr Res 29(2): 249–254
77. Davidovits J (2008) Geopolymer chemistry and applications, 2nd edn. Institut Geopolymere, Saint-Quentin
78. Davidovits J (1994) Geopolymers: man-made rock geosynthesis and the resulting development of very early high strength cement. J Mater Educ 16:91–139
79. Scrivener KL, Kirkpatrick RJ (2008) Innovation in use and research on cementitious material. Cem Concr Res 38(2):128–136
80. Bentur A (2002) Cementitious materials—nine millennia and a new century: past, present and future. J Mater Civ Eng 38:2–22
81. Garboczi EJ, Bentz DP (1999) Percolation aspects of cement paste and concrete—properties and durability. In: Actas de high-performance concrete: research to Practice. American Concrete Institute Spring Convention, Chicago, 14–19 Março, pp 147–164
82. Scrivener KL, Young JF (eds) (1997) Mechanisms of chemical degradation of cement-based systems. Taylor & Francis, London
83. Baghabra Al-Amoudi OS (2002) Attack on plain and blended cements exposed to aggressive sulfate environments. Cem Concr Compos 24(3–4):305–316

Renders

2

Inês Flores-Colen and Jorge de Brito

Abstract

This chapter includes a brief history of coatings and mortars. Then, several classifications are presented, in terms of the main functional purpose, binder type and production site. Renders' performance characteristics, in fresh and hardened state, are described, focusing on requirements, testing methods and standards. Design and construction recommendations are synthetized in terms of materials (binders, aggregates, admixtures and additions/fillers), design details/technical specifications for construction and also characteristics of each coat in the render systems for traditional and industrial renders. Finishing layers are also presented. The pathology and diagnosis of these coating systems are characterised in terms of the common anomalies and probable causes, diagnosis techniques (in laboratory and in situ). Maintenance and rehabilitation strategies are discussed for renders in current and ancient buildings. Finally, American and European standards with renders/plasters and cement-based products are synthetized.

Keywords

Renders • Performance • Design • Construction • Pathology • Diagnosis: maintenance • Rehabilitation • Standards • Cement-based mortars • Lime-based mortars • Testing • Industrial renders • Traditional renders

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M.C. Gonçalves, F. Margarido (eds.), *Materials for Construction and Civil Engineering*, DOI 10.1007/978-3-319-08236-3_2

2.1 Historical Introduction

The first mortars made of lime only might have been used in Jericho, Palestine (7000 AC) [1]. Several studies indicate clearly the use of mortars in construction in the Etruscan epoch (1100–501 AC). At that time the use of terracotta and small-sized stones agglutinated with slaked lime allowed cutting and applying great stone blocks, with little labour [2].

The Romans (800 AC–474 DC) improved this technique, introducing "cement", fine aggregate, capable of being agglutinated by lime, thus making mortars that, confined by stone blocks or filling their joints, conferred the construction great resistance, especially when natural pozzolans were added to lime [2].

After the Roman Empire came a very convoluted period of the Western European history; the Roman civilization did not have such brilliant followers and their technologies were partially lost, so that today little is known about these mortars' composition. However, some written documents remained, named the *Ten Books on Architecture* by Vitruvius [3], an architect contemporary of Julius Caesar. The work of various researchers that have analysed the mortars from this epoch, of which there are countless remains, demonstrates their strength and durability. From experiences that have been made, air lime was the main binder of these mortars [4], and it was very common to find scraps of bricks, roof tiles and other materials with pozzolanic characteristics that conferred a good hydraulic behaviour [5, 6]. The causes of the hydraulicity remained obscure for a very long time, and the reasons why some limes hardened under water are unknown. However, the use of impure limes seems to have been frequent, conferring some hydraulicity, mainly in the cruder mortar works but also in coatings and finishes. The main reason was the use of natural pozzolans—volcanic materials—or artificial ones, such as brick powder and brick fragments [7].

The Romans did not know the chemical and mineralogical composition of the materials they used in construction. However, their mortars showed such a good performance after many centuries that the new material that came up in the eighteenth century was "Roman cement". This material was a superior quality lime, in terms of hardening and water resistance, and anticipated the well-known Portland cement of today [7].

In 1756 John Smeaton pioneered the use of "hydraulic lime" (a form of mortar that will set under water) and developed a technique involving dovetailed blocks of granite in the building of the Eddystone Lighthouse.

It was only after the Industrial Revolution that important scientific works surfaced on hydraulicity and the industrialization of the production of air and hydraulic limes [8]. The discovery of cement by Louis-Joseph Vicat occurred in 1812–1818. From the 1920s on, with the introduction of the concept of hydraulicity and the understanding of natural cement, the distinction was made between air limes, those more or less hydraulic and natural cements [9].

The scientific efforts put into the nineteenth-century studies came together with the creation of artificial Portland cement, in 1824 by Joseph Aspdin (or Aspden), allowing the simulation and control of all its production stages. Besides these qualities, this new material had the advantage of allowing manufacturing mortars of much greater strength and quick setting.

In Portugal, since almost the beginning of the twentieth century with the introduction of Portland cement, there was a progressive decline in the use of lime (in particular air lime) in mortars production and an increasing use of cement, very often as the only binder. This binder allowed greater strength, improved adherence and much faster setting (since the mixed-binder mortars had much higher setting times) [10]. The use of cement and sand mortars also facilitated the organization of the construction site in terms of materials stocking. However, the excessive use of mortars with cement only created another type of problems, associated with excessive shrinkage and consequent cracking of renders.

The emergence, between 1950 and 1960, both in Europe and the United States, of renders based on premixed products was due to the need to suppress the operations of formulation and dosage on-site [11]. At an initial stage these products produced in factories and sold as powder (ready to mix) had a similar composition to that of traditional renders. The first generation of these premixed products resulted directly from the current habits on-site, related with the execution of very strong renders, made exclusively with cement and with high binder contents. These products contained few admixtures, essentially to improve the adherence (resins) and the waterproofing capacity [12].

However, the development of new substrate materials allowed improving the characteristics of these products (e.g. the enhancement of the mortars' water retention or the reduction of the mechanical characteristics through the use of lightweight fillers to apply in aerated cellular concrete masonry substrates). Therefore, the evolution in the manufacturing of these products was towards more deformable mortars (in which part of the cement was replaced with lime, usually air lime, and the reduction in binder was compensated by the incorporation of filler to maintain a good workability) [12].

In the last decades the industry gained a deeper knowledge of the on-site behaviour of these products and on the use of admixtures (e.g. the introduction of more stable air entrainers as a function of the mortar type, the use of water retainers in order to simplify the operations of substrate preparation and the incorporation of lightweight fillers in products for mechanical spraying). Experience has shown that the trend is the formulation of premixed renders with intermediate characteristics, adequate for different types of application [12].

Finally it should be referred that there has been a return to including air lime in the composition of rendering mortars, due first to a better understanding of the problems that resulted from ceasing using it and also to the need to perform rehabilitation works in ancient masonries where the cement mortars have led to unsatisfactory results [13]. The rate of new construction has significantly slowed down in the last few years, while buildings rehabilitation has slightly increased but it has a great growth potential in the near future. In this context, the number of Portuguese national research studies on the specification of hydraulic and air lime and mixed-binder mortars to be applied in ancient buildings (currently called ancient mortars) [14] has been growing, as well as that of studies focused on the

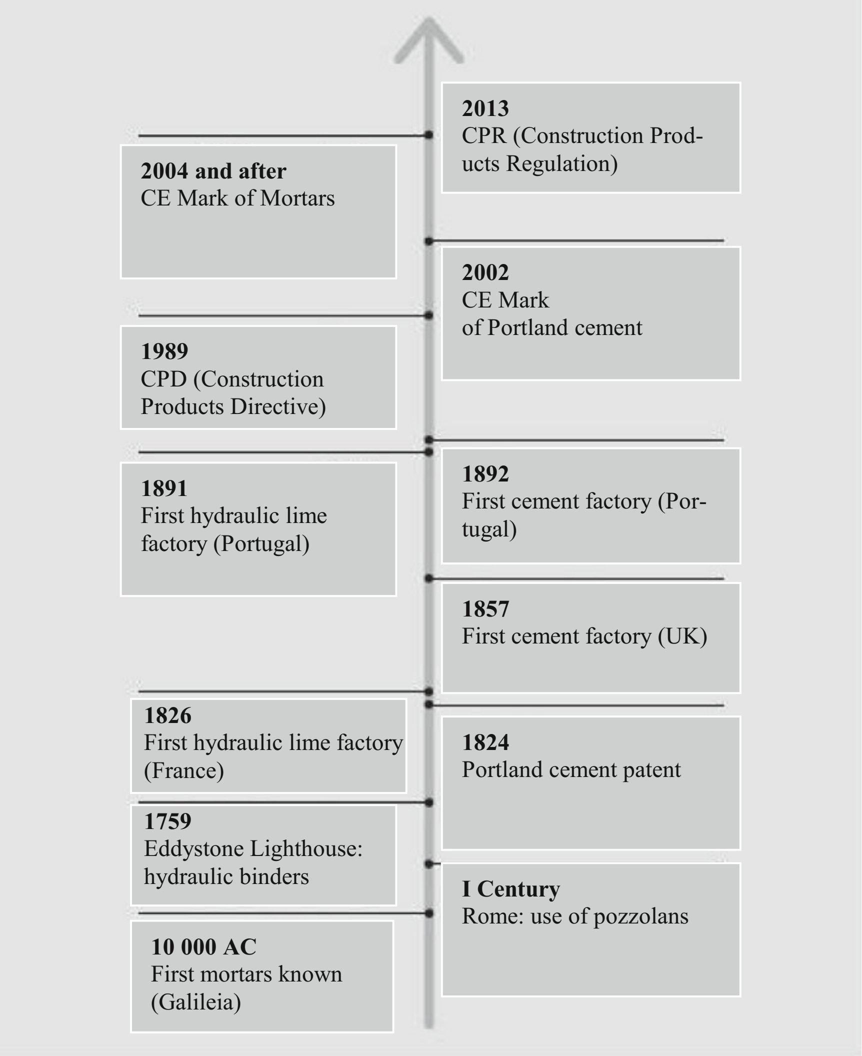


Fig. 2.1 Synthesis of the history of mortars [16]

use of various constituents of these mortars, such as the influence of adding pozzolans to lime mortars [15], or on the procedures related with the production of lime mortars (e.g. the influence of the lime's maturation time on its quality [7]).

Additionally, other challenges concerning the mortars formulation come up, such as improving their energy performance by incorporating insulating compounds or aggregates, in the context of energy efficiency of construction elements, or aspects related to their life cycle, environment and sustainability (recycling and reuse). Figure 2.1 presents a synthesis of the history of mortars, from their onset to CE marking, after 2004 for construction mortars (but compulsory after February 1, 2005 for rendering mortars, through system 4 of evidence of conformity).

It is thus concluded that the subject of construction mortars is much diversified, since various types of constituent materials may be involved, with specific technology. Presently, construction mortars have various uses and may be associated with traditional technologies or competitive new technologies that thrive to answer the present demands at the construction sites, or even integrating maintenance and rehabilitation activities.

2.2 Mortars Classification

Construction mortars are classified in five groups, according to their application scope [11, 16, 17]: masonry bedding mortars, rendering mortars, cement-glues, joint mortars and pavement smoothing mortars (screeds). This chapter is focused on walls coating mortars, currently called renders or plasters (a mixture of one or more binders, aggregates and eventually additions and/or admixtures, used to coat exterior and interior walls; they can be mineral or organic according to the binder's nature; these mortars, with or without water-repellent admixtures, can be finished with ceramics, paints or a variety of finish treatments).

2.2.1 Functional Classification

The classification currently used in Portugal for coating mortars and adopted by LNEC (National Laboratory for Civil Engineering in Lisbon) is focused on their main functions. In exterior coatings, the classification considers the following four categories [18]:

- Watertightness coatings—they have the capacity of guaranteeing by themselves the watertightness of the wall to rainwater; theoretically even if the wall is cracked, this coating type will prevent water entry to the inside (non-absolute criterion, e.g. elastomeric membranes—reinforced synthetic binder coatings—have this capacity up to a given level of cracking of the wall).
- Waterproofing coatings—they provide a significant contribution to the global watertightness of the wall but do not ensure by themselves that watertightness.
- Thermal insulation coatings—their main function is thermal insulation, instead of watertightness; in what concerns their water protection capacity, they are generally watertight or waterproofing coatings.
- Finishing mortars—their main function is to finish the walls, and their contribution to watertightness is of little significant (e.g. water-based paints).

Table 2.1 Classification of walls exterior surface coatings [19]

Functional classification	Main types of exterior walls coatings
Watertightness coatings	Natural stone plates mechanically fastened to the substrate, with cavity
	Plates of other materials mechanically fastened to the substrate, with cavity
	Reinforced synthetic binder coatings
Waterproofing coatings	Traditional renders
	Pre-dosed renders (one-coat or others)
	Mixed binder renders (dement and resin)
	Synthetic binder coatings
Thermal insulation coatings	Claddings of independent discontinuous elements with insulation in the cavity
	Claddings with insulating components
	Coatings applied over insulation (EIFS systems)
Finishing coatings	Claddings of discontinuous elements glued or mechanically fastened without cavity (tiling, decorative tiles)
	Paint coatings

Table 2.1 presents a classification of walls exterior surface coatings [19] where the coatings that are the object of this chapter are shaded, with a functional classification of "waterproofing coatings".

For interior coatings, this classification considers the following four categories [20]:

- Smoothing coatings—they give the wall planeness, verticality and surface regularity.
- Finishing coatings—they give the wall a smoothing complement, also guaranteeing in most cases a pleasant visual aspect.
- Water-resistant coatings—they make up the finishing coat of the walls in locations where water is present frequently or cleaning is wet.
- Decorative coatings—they provide the aspect intended by the users in terms of visual comfort, when the underlying layers do not do so by themselves.

Similarly to exterior coatings, the main types of walls interior coatings dealt with in this chapter are traditional and premixed renders. In this case, interior coatings are classified as "smoothing coatings", since their main function is to provide interior walls with planeness, verticality and surface regularity [19].

2.2.2 Classification According to the Binder Type

In the production of mortars, various types of binders may be used, leading to a classification according to the binder type [11, 20]:

- Slaked air lime and sand mortars—with high ultimate deformation, low shrinkage, friable structure, very slow hardening and wide use in rehabilitation works.

- Natural hydraulic lime and sand mortars—with intermediate characteristics between cement and sand mortars and slaked lime and sand mortars.
- Artificial hydraulic lime and sand mortars—with compressive strength similar to that of natural hydraulic lime mortars and less ultimate deformation.
- Gypsum mortars—mortars made with binder and eventually other binders with weak mechanical strength and sensitive to humidity (used only in interiors).
- Cement and sand mortars—with high strength, great compacity, high shrinkage and stiffness and great propensity to cracking.
- Cement, lime and sand (mixed-binder) mortars—with greater workability, ultimate deformation and porosity and lesser cracking propensity compared to cement and sand mortars; it is mostly the cement that confers strength and the initial mechanical characteristics.
- Mixed-binder mortars, made with mineral and synthetic binder (e.g. polymer) in a proportion over 2.5 %—generally with better characteristics of adherence, deformability, waterproofing capacity and tensile strength; with growing use in walls coatings (to repair existing renders or integrate other coating systems, such as exterior thermal insulation systems, where a thin layer of cement and resin mortar is applied over a thermal insulation substrate).

2.2.3 Classification According to the Properties and/or Purpose

There are classifications used in European normative documents that also include codes associated to the various coatings taking into account their properties and purpose (Table 2.2).

2.2.4 Classification According to the Production Site

In the classification according to the production site, mortars are divided in three groups as follows [17]:

- Industrial mortars—mortars dosed and mixed at the factory; they come "in powder" (requiring only water to be added on construction site) or "in paste" (ready to apply mix).

Table 2.2 Classification according to the properties and/or purpose (EN 998-1: 2010)

Designation	Code
General purpose rendering	GP
Lightweight rendering	LW
Coloured rendering mortar	CR
One-coat rendering mortar	OC
Thermal rendering	T
Renovation rendering	R

- Semi-finished industrial mortars—industrial mortars to be modified on-site, such as:
  - Pre-dosed mortars—their components are dosed at the factory and made available on-site, where they are mixed according to the instructions and conditions of the manufacturer (e.g. multi-chamber silo).
  - Premixed mortars—their components are dosed and mixed at the factory, made available on-site, where other components that the manufacturer specifies or provides as well (e.g. cement) are added.
- Made on-site or traditional mortars—mortars composed by primary constituents (e.g. binders, aggregates and water), dosed and mixed on-site.

2.2.5 Simplified Nomenclature Adopted in This Chapter

In order to simplify the nomenclature in the next sections of the chapter, the following global classification of exterior and interior rendering mortars (renders) is used:

- Traditional renders, dosed on-site and performed according to conventional procedures and mostly manual application
- Pre-dosed mortars, in which the constituents are pre-selected and dosed at the factory, in a mixture provided in powder (in this case it is necessary to add water on-site) or in paste (provided in silos, ready to use), whose application is generally made by mechanical spraying

2.3 Functional Requirements and Performance Parameters

2.3.1 Functional Requirements

The Community Directive relative to construction products, 89/106/CEE of December 21 and 93/68/CEE of July 22, transposed to the national context by Decree-Law 113/93 of April 10, changed by Decree-Law 4/2007 of January 8, establishes the following six essential requirements for building construction works (that include various products, materials and systems): stability (EE1); safety against fire risks (EE2); hygiene, safety and environment (EE3); safety in use (EE4); protection against noise (EE5); and energy savings (EE6), taking into account an economically viable period and current maintenance (durability and adequacy to use). This Directive (CPD) is repealed by the Construction Products Regulation (CPR) No. 305/2011 of the European Parliament and of the Council of March 9, 2011, laying down harmonized conditions for the marketing of construction products and including other essential requirement conditions related with the sustainable use of natural resources. This chapter scopes the requirements of renders in general, with exterior and/or interior application, and the following main requirements [21–23]:

- Protection of the walls against external actions (weather related and resulting from the building's normal use)—a render must adhere to the substrate and have a mechanical strength adequate for that function (i.e. show adequate values of internal mechanical strength; resistance to deformations and dimensional variations; and resistance to abrasion, scratching, shock actions, among others); interior walls confining with pavements must be protected with baseboards, whenever the interior renders of those areas do not have satisfactory resistance to the actions related to the use and maintenance of interior spaces.
- Waterproofing and water resistance of the walls—an adequate resistance to water of various origins (rain, damp, capillary and water vapour); exterior renders, in over-the-ground walls must promote the passage of water vapour generated in the building's interior to its exterior, even though guaranteeing waterproofing against rainwater; in the case of inner surfaces where there are water devices, renders must be protected with wainscots at least 1.5 m high.
- Walls finishing—a render must provide coated walls with a regular and plane defect-free surface, with characteristics that facilitate their cleaning, taking into account the users' visual comfort and the aesthetic value of the walls.
- Adequate durability, bearing in mind maintenance—a render must guarantee the previous functions for a period of time (service life) compatible with the difficulty and cost of the in-service maintenance actions; therefore, the capacity to obtain adequate performance levels depends a lot on the guarantee of geometric and physical-chemical compatibility between the render, its substrate and the final finish.

On the other hand, the contribution of renders is not as significant as that of other wall elements (masonries or other types of coating) in the following situations [21]:

- Fire safety—renders only contribute to complying with the fire reaction of the surfaces' constituent materials because they are non-combustible materials (mineral renders with little organic matter in their composition); an important role in fire resistance of coated walls is assigned to masonries; renders belong to fire reaction Euroclass A1, because they have a small content of organic matter according to EN 998-1: 2010 and the 2000/147/CE Directive.
- Protection against noise—the extra sound reduction resulting from adding a coating to a wall is usually not important, unless it is a lightweight wall [24].
- Economy of energy and heat retention—a mortar coating has a limited effect on heat transmission through a current external wall, since its thermal conductivity is relatively high and its thickness is small; the contribution to thermal insulation, treatment of thermal bridges and thermal inertia of opaque surfaces becomes significant when a coating system including an insulation layer is applied (e.g. coating over insulation or coating of hydraulic binders with aggregates of an insulating material) (BRE Digest 196; Cahier 1633); rendering mortars have thermal conductivities between 0.07 and 1.28 W/m K, according to

the material's density, which is given in EN 1745: 2012. The requirements of EN 998-1: 2010 include: (a) declaration of the tabled values (VT) for mortars GP, LW, CR, OC and *R*; (b) categories $T1 \leq 0.1$ W/m K and $T2 \leq 0.2$ W/m K for thermal insulation mortars (*T*).

Finally, the non-negligible contribution of renders to the environment is highlighted, in terms of recycling and reuse of mortars during their life cycle, accounting for the environmental impacts that these mortars have on the environment during their production, application and/or demolition (e.g. a deficient control of the final destiny of washing water of the mixers and of the waste resulting from the production of traditional cement mortars contributes to the contamination of natural resources, namely the pollution of water and soil).

2.3.2 Prescriptive Specification/Performance-Based Formulation

For a proper evaluation of the adequacy to use of applied renders, a performance-based approach must be followed comprising three main steps:

- Definition of the functions to be performed by the render (functional requirements)
- Identification of the most relevant performance characteristics (i.e. performance parameters quantifiable whenever possible and capable of being monitored in service)
- Definition of the methods of quantification and evaluation of the previous parameters, resorting to in situ or laboratory tests

In fact, the application of this approach is easier in non-traditional renders because there is backing from harmonized European standards (requirement standards) or homologation/application documents produced by LNEC (additional requirements) or other national entities. Concerning traditional renders, their specification still puts emphasis on a prescriptive formulation, through the recommendation of volumetric or weight proportions.

According to EN 13914-1:2005, the choice of the render type, its composition, the number of coats and their thickness depends on the intended aspect, the exposure conditions, the nature of the substrate and the requirements. To specify the composition (proportions), it must be stated whether they are determined by weight or by volume and whether dry or damp sand is used. This European standard does not define proportions, due to the technological and climatic differences between the various countries. However, it typifies mortar mixes (used in exterior renders), as a function of the substrate:

- Strong mixes—they yield strong, impermeable, high shrinkage mortars, consequently highly susceptible to cracking; their use should be restricted to stronger substrates.

- Moderately strong mixes—they probably lead to satisfactory results in most renders; they are more permeable and have less drying shrinkage than the former ones; their strength is adequate in most situations; the mixes with lower cement content are less prone to cracking, but may not be strong enough to withstand severe abrasion.
- Weak mixes—adequate for weak substrates under protected conditions and for repair work of less compact lime-based renders.

Table 2.3 presents a synthesis of the volumetric proportions of the base and finishing coats of renders applied on brick masonry substrates [20], taking into account the type of finish of the rendered surface and the exposure conditions.

It is stressed that prescriptive specification, even though providing relevant information (about the various coats, exposure conditions, types of substrate and types of finish), is clearly insufficient for periodic monitoring of the in-service performance [21]. Therefore, technical documentation has gradually changed from prescriptive to performance based, in which the functional requirements are translated into quantifiable performance characteristics.

2.3.3 Performance Parameters and Test Methods

Based on the literature analysed, a set of performance parameters was defined for coating mortars at the application phase, in the fresh state and of transition to hardened state, and the complete coating system (constituent layers and eventual surface finish), in the hardened state.

2.3.3.1 Workability

The workability is a fresh-state mortar's characteristic that allows its proper application (compacity and yield), its capacity to adhere to the substrate and the possibility of modifying the surface to achieve the intended finish. In practice this is the most determining property for renders on-site, since unlike concrete wall rendering mortars do not generally require great strength. This property is determining for the in-service performance of renders since if, on the one hand, it allows and facilitates their application on-site, in reality it conditions the render's performance at other levels, namely in what concerns shrinkage and waterproofing [26].

This contradiction is easy to perceive if one considers that, in order to get a better workability, a greater water content relative to cement or an increase in the sands fines content is needed. At the drying stage, however, the greater the amount of water lost, the bigger the consequent volume loss and the associated shrinkage. On the other hand, an unbalanced water/cement ratio may lead to an excessively wet render and a deficient curing with implications on the cohesion of the mortar [26].

To control this problem there are today in the market admixtures that promote a mortar's workability (plasticizers and air entrainers that simultaneously improve the mortar's behaviour in terms of freeze/thaw cycles), but as various authors stress their effects are not always predictable and therefore it is important to test them

Table 2.3 Coating systems adequate for brick masonry substrates [20]

Type of finish of the rendered surface	Exposure conditions	Base coats		Finishing coats
Smooth floated (wooden float)	Severe (unprotected exposure to rain water driven by wind)	1:3–4	1:5–6	1:5–6
		1:0.5:4–4.5	1:1:5–6	1:1:5–6
	Moderate (partially protected walls)	1:5–6	–	1:5–6
		1:1:5–6		1:1:5–6
	Favourable (regions with little rain and protected walls)	1:5–6		1:5–6
		1:1:5–6		1:1:5–6
Rough with fine texture	Severe (unprotected exposure to rain water driven by wind)	1:5–6	1:5–6	1:5–6
		1:1:5–6	1:1:5–6	1:1:5–6
	Moderate (partially protected walls)	1:5–6	–	1:7–8
		1:1:5–6		1:2:8–9
	Favourable (regions with little rain and protected walls)	1:5–6		1:7–8
		1:1:5–6		1:2:8–9
Exposed pebble	Severe (unprotected exposure to rain water driven by wind)	1:3–4	1:3–4	1:3–4
		1:0.5:4–4.5	1:0.5:4–4.5	1:0.5:4–4.5
	Moderate (partially protected walls)	1:3–4	–	1:3–4
		1:0.5:4–4.5		1:0.5:4–4.5
	Favourable (regions with little rain and protected walls)	1:3–4	–	1:3–4
		1:0.5:4–4.5		1:0.5:4–4.5

Note: The upper proportions refer to cement and damp sand mortar and the lower ones to cement, lime and damp sand mortars [25]

on-site before their application [27, 28]. For example, using 0.15 % of superplasticizer in a hydraulic lime mortar contributes to a relatively stable increase of workability. The influence of air entrainers depends on the amount added, and the use of only 0.10–0.15 % has been proved to contribute to the increase of workability of air lime mortars [29].

To measure the workability of mortars, a rheometer is sometimes used (for the analysis of the mortar's rheology, i.e. the study of its fresh-state deformation and flow, including the properties that influence the mixing, transportation and application process), even though the use of the slump flow test (EN 1015-3: 1999) (Fig. 2.2) is more frequent.

Fig. 2.2 Slump flow test to evaluate the consistency of fresh mortar [30]

2.3.3.2 Water Retention

The water retention, characteristic of a fresh-state mortar, translates the mortar's capacity of retaining the mixing water, when subjected to the substrate's suction, allowing its normal hardening [17] in contact with absorbent surfaces. This property is important for the adequate cement hydration and for the chemical reactions to occur under the best conditions during curing. Its control allows prolonging the plastic state of fresh mortar, increasing the workmanship's productivity [29].

When compared to cement mortars, lime mortars have a high water retention capacity, and adding a small amount of cement to these mortars is enough to drastically reduce this property [31].

From the analysis of existing requirements [21] for current rendering mortars it is found that water retention (U) must be high ($U \geq 80$ %), and there are some specific conditions that require an even higher value, such as drier weather during application ($H_r < 80$ %) or high temperatures (25 °C $< T <$ 30 °C) with strong wind. The type of substrate is also relevant to this parameter, i.e. the render's water retention must be higher than the usual ($U \geq 91$ %) in more absorbent or weaker substrates, but the maximum value must be controlled in little absorbent substrates ($U \leq 94$ %). The water retention (%) is measured in laboratory (prEN1015-8: 1999) (Fig. 2.3).

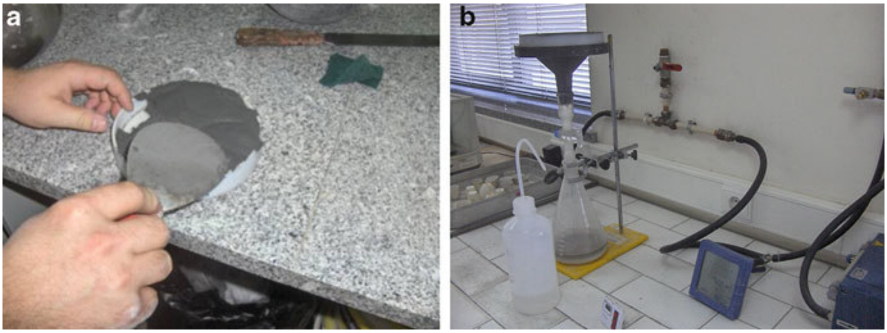


Fig. 2.3 Water retention test in cementitious mortar, in the fresh state

2.3.3.3 Shrinkage

Shrinkage or contraction is a characteristic related with the decrease of volume of a mortar, either by mixing water evaporation or by phenomena related to hydration and carbonation of the binder [29]. Knowing the shrinkage phenomenon and its evolution is extremely important to control its causes and try to minimize its effects, which range from micro-cracking to cracking of the mortar, with consequences on loss of waterproofing capacity, negatively affecting this coating's durability [32].

Global shrinkage occurs by desiccation, hydration and carbonation throughout the mortar's service life, with a continuous interaction between these phenomena, almost always resulting in a contraction. In mortars, thermal-related shrinkage is not as relevant, due to their small thickness. These phenomena are now succinctly described [18, 32]:

- Desiccation—it corresponds to the exit of water from the capillary vases and then from the smaller pores, leading to contraction coupled with mass reduction, leading to water loss that may reach 22 % of the cement paste [33]. Desiccation is mostly due to evaporation and absorption by other elements in contact with the coating, namely its substrate [34]; this type of shrinkage is partially reversible.
- Hydration—it corresponds to shrinkage from hydration reactions, with the formation of new chemical compounds, coupled by exothermy and self-desiccation (consumption of the water from the pores) in the resulting chemical reactions: this type of shrinkage, due to the importance of the chemical component, is mostly irreversible.
- Carbonation—it is due to the combination of carbon dioxide from the atmosphere with the hydrated components of cement (a reaction with water release, whose rate depends on the air's hygrometry, with a maximum of 50 % of H_r [34]), in particular calcium hydroxide, which originates solid products such as calcium carbonate, whose global volume is lower than the sum of the volumes of the cement components that are used in the reaction, but whose mass is higher; the renders are very prone to carbonation, due to their small thickness and high permeability to gases that favour the combination of carbon dioxide from the air

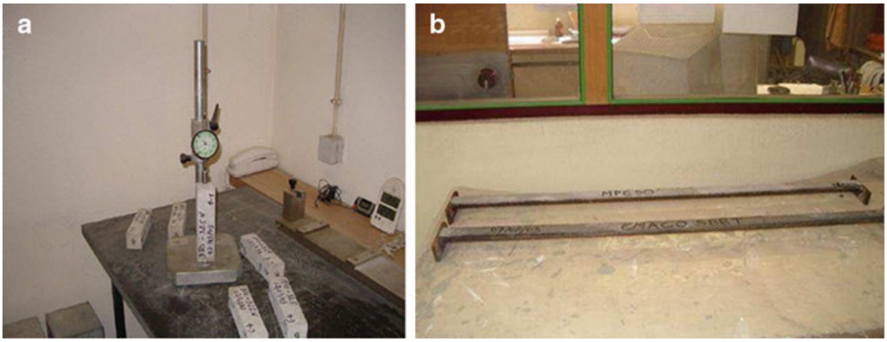


Fig. 2.4 Free shrinkage test with (**a**) measurement of the relative displacements of the tops; (**b**) bracket test to evaluate the render's cracking propensity [35]

(however, this permeability decreases in depth, slowing down carbonation of the inner layers relative to that of the external layers).

The relative predominance of the preceding phenomena depends on the render's age: desiccation influences global shrinkage and is much more influencing after the beginning of setting (a period when shrinkage by desiccation is much higher than shrinkage by hydration) and after hardening (when hydration is practically over and causes little deformation). Right after the end of setting, the interaction between these two phenomena is important. The dimensional changes due to hydration are preponderant during hardening. Finally, shrinkage by carbonation occurs throughout the mortar's life, becoming relevant, the more permeable to air the mortar is and the more favourable the environmental conditions are to the carbonation reaction [32].

The analysis of shrinkage in laboratory has been made by measuring the free and/or restricted shrinkage, representing the mortar's volume reduction, without (free movement) or with substrate (restricted movement), during its hardening [17]. The free shrinkage of the render must be moderate and the restricted shrinkage medium to weak, for a better resistance to cracking.

In the analysis of free shrinkage, one-dimensional variations are measured in specimens in moulds with devices that allow measuring the relative displacements of the tops, along the longitudinal axis, and their weight variation is evaluated (prEN 1015-13: 1993) (Fig. 2.4a). It is frequent to measure linear shrinkage by applying mortar inside a metal bracket-shaped profile [30, 35] (Fig. 2.4b).

Renders are applied on a substrate, generally very stiff, to which they adhere. As the mortar dries, shrinkage develops, normally under very unfavourable conditions: fast evaporation and suction of the substrate, which is restricted by the adherence to the substrate, inducing stresses in the mortar. Therefore, mortars are subjected to stress fields that result from restricted shrinkage, whose determination implies knowing the capacity of relaxation of the mortar. The stress installed within the mortar varies over time, due to the variation of shrinkage and modulus of elasticity and the influence of this ratio, but the tensile strength of the mortar also varies with time, depending on the degree of hydration [32].

A test procedure (FE Pa 37:1998, methodology to evaluate cracking susceptibility of renders) was developed in LNEC that includes the design and execution of specific equipment capable of restricting the shrinkage of a mortar specimen, measuring the forces generated. The results of this test allow parameterizing the mortar's cracking susceptibility, taking into account the following coefficients [18]:

- Safety coefficient concerning the opening of the first crack (CSAF), determined as follows:

$$\mathrm{CSAF} = \frac{R_\mathrm{t}(t)}{F_\mathrm{r}(t)}$$

where R_t = tensile strength of the mortar and F_r = force generated by the restricted shrinkage.

- Coefficient of resistance against the evolution of cracking due to restricted shrinkage (CREF), determined as follows:

$$\mathrm{CREF} = \frac{G}{F_{\mathrm{r\ max}}}$$

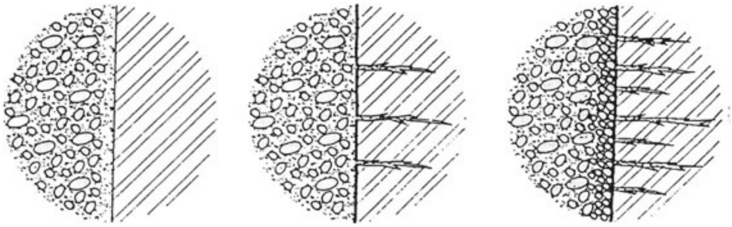
where G = failure energy and $F_{\mathrm{r\ max}}$ = maximum force generated by the restricted shrinkage.

The cracking propensity of renders made on-site is measured by their class of susceptibility to cracking: medium ($\mathrm{CSAF} \geq 1$ and $0.6\ \mathrm{mm} \leq \mathrm{CREF} < 1\ \mathrm{mm}$) or weak ($\mathrm{CSAF} \geq 1$ and $\mathrm{CREF} \geq 1\ \mathrm{mm}$) [18].

2.3.3.4 Adherence to the Substrate

Adherence is the property that allows render to withstand normal and tangential stresses acting in the interface with the substrate, even after the hardening process. The adherence of render to its substrate is fundamental to fulfil the functions of waterproofing and protection of the walls over time, as well as the adherence between constituent coats of the coating system. Furthermore, it greatly influences the cracking resistance, in the sense that it conditions the stress distribution within the mortar [18, 36].

In traditional admixture-free renders, adherence occurs by penetration of the mortar's fine elements into the substrate's pores, forming a system of "mechanical anchorage" [37]. Therefore, the adherence is influenced mostly by aspects related to both the rendering mortar and the substrate. The richer in binder the mortar and the greater its fine content, the greater its adherence will be. However, such contents lead to greater cracking by shrinkage that may by itself cause loss of adherence. The purpose is then to find a balance between these two factors [38]. In non-traditional renders it is possible to add admixtures that work as adherence promoters,



Loss of adherence due to the low absorption of the substrate

Adequate adherence due to mechanical bonding conferred by an adequate absorption

Desiccation of the mortar due to excessive absorption of the substrate

Fig. 2.5 Mechanical adherence of the render, according to the substrate's suction [18]

improving this characteristic in the hardened state; however, the adherence of these coatings is still sensitive to the application conditions and the substrate's preparation.

Since adherence depends on the penetration of the mortar's laitance into the substrate, it seems natural that the latter's porosity and capillary suction are also influential. Therefore, adherence will be better in absorbent substrates since they allow a better mechanical bonding. However, an exaggerated absorption capacity will tend to rapidly desiccate the coating, stopping the hydration of its constituents and favouring the formation of a pulverulent interface (Fig. 2.5). This eventuality may be prevented by the previous humidification of the substrate, even though not excessive to the point that it prevents mechanical adherence from occurring [18].

Still concerning the substrate, rough textures confer better adherence, because they increase the area of contact between render and substrate [39]. The compatibility with the substrate, in terms of strength and modulus of elasticity, is also important, in order to prevent the generation of stresses in the interface that impair adherence. Finally, the coating's curing must also be careful, in order to prevent the generation of harmful stresses caused by shrinkage [40]. An expedient method of evaluating adherence consists on tapping the surface (non-adherent areas have a "hollow" sound) [41]. However, this technique is only qualitative and that is why generally the render adherence (of the coat in contact with the substrate) is evaluated through tensile pull-off tests (Fig. 2.6), in dry and damp conditions (N/mm^2), according to EN 1015-12:2000, or after an accelerated ageing test (EN 1015-21: 2002).

This technique's drawback is that it is locally destructive, but it allows quantifying the adherence stress and the failure type—cohesive (in the mortar or the substrate, because of the lack of "internal cohesion") or adhesive (in the interface between them, because of the lack of "adherence") (Fig. 2.7). The evaluation of the failure type allows analysing the balance between the render's strength and its adherence to the substrate (when failure is predominantly cohesive in the tests, the material' strength is smaller) [21].

Cementitious renders generally have an adherence stress (f_u) between 0.3 and 0.5 N/mm^2; existing requirements demand a value above 0.3 N/mm^2 or cohesive failure (Table 2.4) [42].

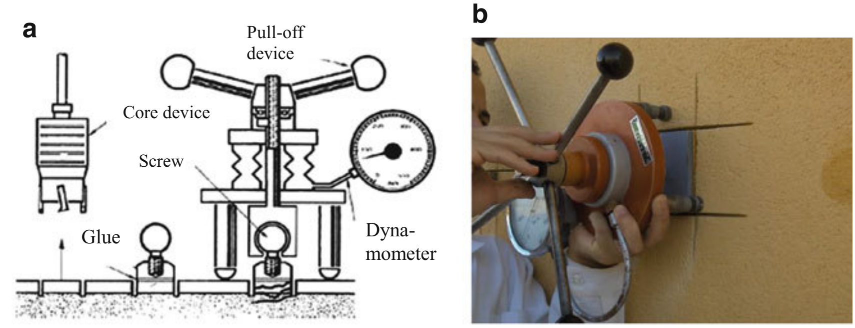


Fig. 2.6 (**a**) Pull-off equipment [18]; (**b**) test in cementitious mortar

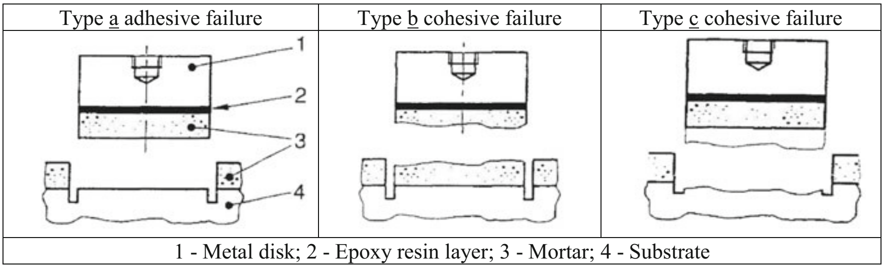


Fig. 2.7 Types of failure after pull-off test (EN 1015-12: 2000)

Table 2.4 Adherence requirements for mortars [18, 21]

Requirements	Reference
$f_u \geq 0.3$ N/mm^2 or cohesive failure	LNEC report 427/05
$f_u \geq$ VD (value declared by the manufacturer) and a cohesive type of failure	EN 998-1: 2010
$f_u \geq 0.3$ N/mm^2, and none of the individual values lower than 0.2 N/mm^2	DTU 26.1: 1994 (NF P 15-201-2)
$f_u \geq 0.3$ N/mm^2, for renders with painting or ceramics	NBR 13528: 1995

2.3.3.5 Internal Mechanical Resistance

The internal mechanical strength of a render concerns its capacity of going through an internal hardening process to make it capable of withstanding mechanical actions and the associated stresses [37]. The mortar's strength is a function of the induced stress level and of the resistance characteristics of the material. In principle, a mortar's strength grows with its binder's content. However, an excess of binder leads to high shrinkage and to cracking of the mortar. So that the mortar is resistant to cracking, it must have a high tensile strength and a low modulus of elasticity, thus better withstanding the stresses installed [10, 18].

Fig. 2.8 (**a**) Strength test equipment [30]; (**b**) flexural strength test; (**c**) compressive strength test

Likewise, the greater the rendering mortar's compacity (that depends on the incorporated air content), the greater its resistance to actions and stresses; the lower the incorporated air content, the more compact the mortar is and greater the apparent bulk density and the internal mechanical strength and the modulus of elasticity are [43].

The internal mechanical strength of a rendering mortar is determined in laboratory, by analysing the compressive and flexural strength of prismatic specimens (Fig. 2.8):

- Compressive strength (N/mm^2)—value at failure of a mortar (in hardened state) determined by applying a compressive force in two opposite points [17], at 28 days (EN 1015-11: 1999)
- Flexural strength (N/mm^2)—value at failure of a mortar, determined by applying a bending force in three points [17], representing the bending stresses that lead to cracking of the mortar, at 28 days (EN 1015-11: 1999)

Cementitious mortars have compressive strength values (R_c) between 2 and 10 N/mm^2, depending on the mortar type (Table 2.5) [42]. The lower limit is adequate for substrates with a weaker mechanical strength; in current masonry, the render's compressive strength should be medium, with values above 4 N/mm^2 [21]. However, values below 2 N/mm^2 may be used in the case of more specific mortars, such as those for renovation or thermal insulation; for renders applied at the bottom of walls, this parameter's requirement is higher ($R_c \geq 6$ N/mm^2) (EN 13914-1:2005).

In the technical specifications the compressive strength of air lime renders does not exceed 1.0 N/mm^2, while in hydraulic lime renders this parameter has an upper limit of 2.5 N/mm^2 [44].

The tensile strength of cementitious mortars is variable but preferably medium to guarantee good cracking resistance (427/05 from LNEC) [45]. In the technical specifications the flexure strength falls between 1.5 and 3.5 N/mm^2 [21]. The lower limit is recommended in the following situations: walls exposed to shocks and deterioration, basement walls, up to 3 m and over 18 m above the ground and application in cold weather and sprayed finish. However, the flexure strength must be higher in the following specific situations: wall exposed to shocks near a public

Table 2.5 Renders' compressive strength requirements [18, 21]

Requirements	Reference
$1.5 \leq R_c \leq 5.0$ N/mm^2 for renovation and thermal insulation mortars	EN 998-1: 2010 (Classes CSI, CSII, CS III, CS IV)
$3.5 \leq R_c \leq 7.5$ N/mm^2 for lightweight mortars	
$R_c \geq 6.0$ N/mm^2 for general use and one-coat mortars (in any case, the mortar must not have a higher strength than the masonry)	
$R_c \geq 2.5$ N/mm^2 for high-strength mortars	DIN 18550-1: 1985[a]
$R_c \geq 1.0$ N/mm^2 for moderately hydraulic lime mortars	
$R_c \leq 2.5$ N/mm^2 for hydraulic lime masonry mortars	
$R_c \leq 10.0$ N/mm^2 for cement-based mortars	
$R_c \geq 12.0$ N/mm^2 for strong and high shrinkage mortars	BS 5262: 1991[b]
$R_c \geq 6.0$ N/mm^2 for moderately strong mortars	
$R_c \geq 4.0$ N/mm^2 for average-strength mortars, less prone to cracking	
$R_c \geq 6.0$ N/mm^2 for low- to moderate-strength mortars	

[a] Due to CE marking/ European standards, these documents have been replaced by DIN V 18550:2005-04; DIN EN 998-1:2010:2010-12

[b] The same occurs here, i.e. BS EN 13914-1:2005 replaces these BS standards

pathway and/or in zones with concentration of people, wall exposed to vibrations ($R_t \geq 2.7$ N/mm^2) and renders with ceramic finish ($R_t \geq 2.0$ N/mm^2). On the other hand, this characteristic must be limited, particularly in very absorbent substrates ($R_t \leq 2.7$ N/mm^2), application with dry or hot weather ($R_t \leq 3.5$ N/mm^2) and damp weather or sprayed finish ($R_t \leq 4.5$ N/mm^2).

Finally, the dry bulk density in the hardened state (kg/m^3) is also of interest, corresponding to the ratio between the dry material's mass and its volume after 28 days of curing; the volume can be measured by the size of the specimens, according to *Cahier* 2669-4 from CSTB, or based on the saturated mass and its hydrostatic weight (EN 1015-10:1999).

Like the compressive strength the density is ranked in classes. Therefore, the value declared by the manufacturer for pre-dosed renders is an important requirement in terms of design specification. According to the technical specifications, there are factors that contribute to a greater demand from this parameter [21], such as a wall exposed to shocks near a public pathway and/or in zones with concentration of people; application in walls up to 3 m and over 18 m above the ground ($M_{ap} \geq 1{,}200$ kg/m^3); basement walls or application in cold weather ($M_{ap} \geq 1{,}400$ kg/m^3); and walls exposed to vibrations ($M_{ap} \geq 1{,}600$ kg/m^3). The type of finish of the rendered surface also conditions the value of the bulk density, namely in increasing order: floated ($M_{ap} \geq 1{,}000$ kg/m^3), scraped or dry dash ($M_{ap} \geq 1{,}200$ kg/m^3) and sprayed ($M_{ap} \geq 1{,}400$ kg/m^3). On the other hand, the bulk density that may reach values around 2,000 kg/m^3 (EN 1745:2012) must be limited in renders applied in substrates whose mechanical strength is very weak ($M_{ap} < 1{,}400$ kg/m^3) or that are very absorbent ($M_{ap} < 1{,}600$ kg/m^3).

2.3.3.6 Cracking Resistance/Deformation Capacity

The distribution, nature, size and depth of cracking condition several aspects of the service life of rendering mortars, namely their waterproofing capacity; the chloride penetration rate; and in some cases, when there is differential shrinkage of the various render surfaces, their adherence to the substrate [26]. Their emergence is due to the coating being unable to withstand the stresses installed (generally tensile), which result from the separate or simultaneous action of the following situations: substrate movements, temperature changes, vibrations or shocks, expansive chemical reactions (carbonation or sulphate attack) and physical changes (freezing water or soluble salts crystallization) [18]. Therefore, renders must have a good deformation capacity (the ability of the rendering mortar to deform without failure), so that no cracking or micro-cracking occurs that compromises the adherence, waterproofing and in-service performance capacity (durability).

This deformation capacity of hardened render is conditioned by the modulus of deformation or of elasticity, shrinkage and tensile strength [18]. The greater the render's modulus of elasticity, coupled with its internal cohesion, the better its capacity to withstand external aggressions will be, resulting, for example, from use—a high modulus of elasticity also allows a better resistance of the render to stresses generated in the interface with the substrate that arises from the drying and shrinkage process of this material. However, the evaluation of the deformation capacity should not be done based solely on the modulus of elasticity, since this represents the ratio between existing stress and the deformation produced by that stress, thus giving no indication about the failure deformation.

The modulus of elasticity may be determined through static and dynamic tests, depending on application rate if the actions and the way the response are measured. The static modulus of elasticity corresponds to the slope of the stress-deformation graph, obtained by loading a specimen and simultaneously measuring the deformation. On the other hand, the dynamic modulus of elasticity corresponds to very small instantaneous deformations and is considered equal to the initial tangent module determined in the static test and therefore greater than the static modulus of elasticity [46]. The dynamic modulus of elasticity (E_d) can be determined resorting to the ultrasonic pulse velocity or the frequency of resonance of the mortar (Fig. 2.9), since these parameters directly depend on the "elasticity" of the material.

Cementitious rendering mortars have dynamic modulus of elasticity (E_d) values ranging from 3,500 to 10,000 N/mm^2. The highest values are recommended in coatings frequently acted by shocks or vibrations, while the lowest values are adequate for weaker substrates (Table 2.6) [42].

Various studies refer that the dynamic modulus of elasticity of lime mortars, with a long slaking period and 60 days of curing, ranges from 1,150 to 2,050 N/mm^2 [47]; for air lime mortars (volumetric proportion 1:3) it is around 2,350 N/mm^2 and for moderately hydraulic mortars around 2,330 N/mm^2 [48].

In traditional renders, which are multi-coat systems, the application of superimposed layers with characteristics that vary from the substrate to the surface reduces the occurrence of cracking and the probability of coincidence of the cracks

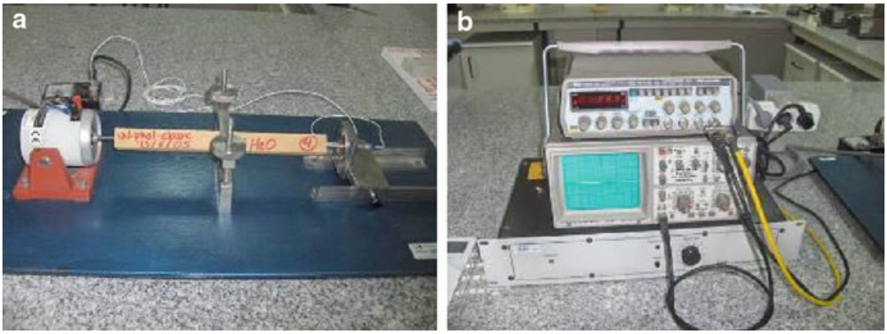


Fig. 2.9 (**a**) Specimen under longitudinal vibration in both sides; (**b**) measurement of the resonance frequency to determine the dynamic modulus of elasticity [21]

Table 2.6 Premixed mortar deformation capacity requirements [21]

Requirements	Reference
$E_d \leq 10{,}000$ N/mm^2	LNEC (report 427/05)
$E_d \leq 10{,}000$ N/mm^2 for current mortars	MERUC classification for pre-dosed mortars (CSTBat R T 18/02) Cahier 2669-4
$E_d \geq 5{,}000$ N/mm^2 for wall coatings exposed to shocks and deterioration	
$E_d \geq 7{,}500$ N/mm^2 for coatings in locations near a public pathway with circulation of people	
$E_d \leq 10{,}000$ N/mm^2 for coatings with very absorbent substrates	
$E_d \leq 7{,}000$ N/mm^2 for coatings with substrates of very weak mechanical strength	
$E_d \geq 12{,}000$ N/mm^2 for coatings in walls exposed to vibrations	

in between layers [20]. In pre-dosed renders, the single coat may aggravate the effects of the emergence of cracking; however, these products include admixtures, e.g. water repellents, which stop water from entering their structure, even if there are some types of micro-cracks.

2.3.3.7 Surface Resistance

Impact and friction actions lead to premature degradation of the render, under given in-service conditions. Therefore, the surface of façade renders must withstand the actions resulting from normal occupation and circulation, such as those associated with the users' mobility and current cleaning and maintenance operations, without significant deterioration (loss of planeness and occurrence of defects).

The surface resistance will grow with the render's cohesion. In principle, traditional mortar coatings have a resistance to shock capable of withstanding actions associated with normal use. Besides risk situations, there are no specific reasons to evaluate the surface resistance except when the coatings are applied in

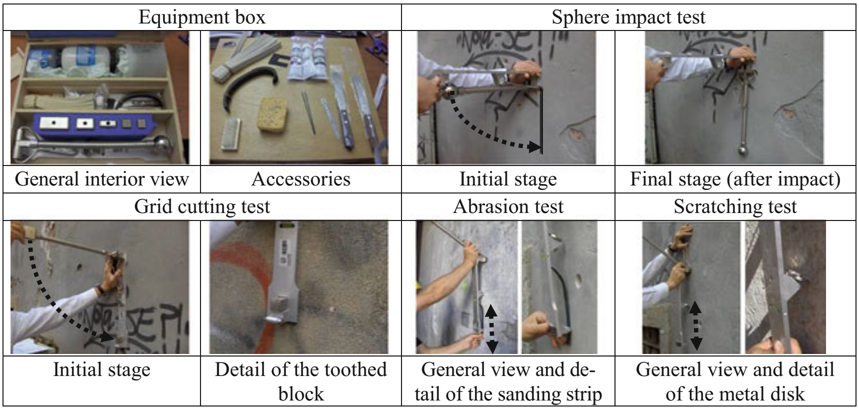


Fig. 2.10 *Martinet Baronnie* equipment and corresponding test techniques [21]

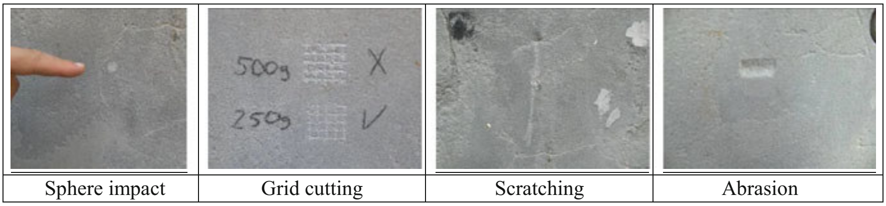


Fig. 2.11 Illustration of measuring parameters [21]

very thin coats, such as in one-coat coatings, or on very deformable substrates, or yet still when used as decorative coatings without any other finishing coat [49].

The evaluation of this property is made using tests of hard body impact resistance, scratching and abrasion and there are several test techniques. In this section the *Martinet Baronnie* test technique is highlighted for the evaluation of the surface resistance of wall renders. With this technique, this property is evaluated in terms of hard body tests, cutting resistance (grid cutting) and impact resistance (sphere impact), taking into account the minimum impact energy (*E*) that the coating must withstand, relative to the damage caused. The various tests and the measuring parameters are summarized in Figs. 2.10 and 2.11:

- Dent diameter—the result of the sphere impact test is expressed by the diameter (mm) of the dents resulting from five hits (FE Pa 25: 1980 from LNEC—test procedure; for further literature about this technique, see reference [49]).
- Grid cutting index—the result of the grid cutting test is expressed by the numerical value of the highest mass that the coating withstands, i.e. without scaling or debonding of the little grid squares; it can be equal to 0, 250, 500 or 1,000; the “0” value is assigned to coatings that do not withstand the cutting action with the smallest mass, 250 g (FE Pa 26: 1980 from LNEC—test procedure; for further literature, see reference [49]).

- Scratching index—the result of the scratching test is expressed by the numerical value (0, 250, 500 or 1,000) of the highest mass that the coating withstands, i.e. even though there may be scratching, there is no detachment (FE Pa 27: 1980 from LNEC—test procedure; for further literature, see reference [49]); a coating that has detachment traces in the least severe test (without any additional mass in the arm of the *Martinet Baronnie* device) is classified as "null", from the point of view of scratching resistance; some studies refer as measuring parameters the depth of the resulting groove, the amount of detached material (g) or the number of little squares damaged.
- Abrasion index—the result of the abrasion test is expressed by the numerical value (0, 250, 500 or 1,000) of the highest mass that the coating withstands, i.e. the friction action does not affect the substrate in a uniform way; a coating that does withstand the friction action without any additional mass is classified as "null"; some studies refer measuring the depth of the resulting groove and the amount of detached material (g) or even a ratio between that amount and the coating's thickness (NT BUILD 281: 1984).

The requirements for surface resistance of interior renders are developed in the gypsum plasters chapter, in terms of gypsum-based coatings' surface resistance.

2.3.3.8 Water-Related Performance

Renders are porous mortars, through which water can penetrate by capillarity or permeability, according to the pores' size, mostly when wind and rain occur simultaneously. This possibility implies considering the waterproofing of the render and its drying capacity in crack-free areas, besides the minimization of water entry through surface cracking [26].

A porous coating with rough finish, with thickness and composition adequate to the weather exposure type, has the right conditions to retain uniformly the rainwater in its whole surface and lose it again by evaporation, when the weather conditions improve; a small porosity (very compact render, with high content of binder) is associated to significant cracking by shrinkage, allowing a great deal of water to be washed through the cracks [20].

A render must allow water vapour exchanges between the substrate and the environment (resulting from the construction works, from the absorbed water or hygrothermal exchanges between the inner and the outer space), minimizing the occurrence of condensations on the render and substrate's surfaces. Additionally the water vapour permeability of the finishing coat—especially in the case of paints—must be accounted for, since it functions as a first barrier against water entry into the render and it also allows the wall to "breathe" as a result of the human activities within [26].

The waterproofing capacity of the renders, concerning the water that penetrates them due to the effect of rain and wind acting simultaneously on their surface, is defined as its capacity to (FE Pa 38: 1999, from LNEC—waterproofing test): (a) delay the instant when water reaches the substrate; (b) limit the water amount

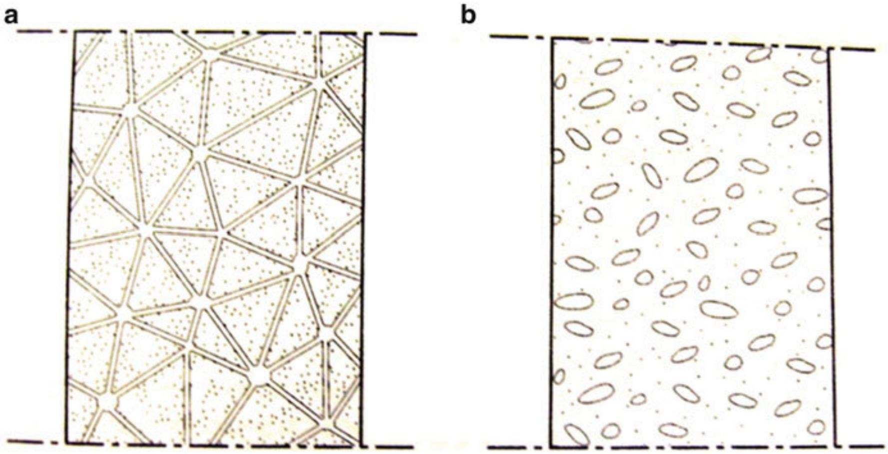


Fig. 2.12 (**a**) Open and (**b**) closed porosity [50]

that reaches the substrate; and (c) retain the water near the substrate for the shortest possible period of time, favouring the drying of the coating.

In this context, the parameters concerning the water-related performance of renders, with emphasis on exterior renders, are porosity/porometry, capillarity, water permeability and water vapour permeability.

Porosity/Porometry

The durability of mortars is related to their porous structure (number of pores and their connectivity) and porometry (pores' distribution and size); these properties influence the water performance of renders in terms of the way the wetting phase (absorption) and the drying phase (evaporation—related to water vapour permeability) progress [29, 51].

The nature, importance and layout of these pores allow defining different types of porosity: global, closed and open porosity (Fig. 2.12). Global porosity is the ratio between the volumes of pores within the mortar and global volume EN 1015-7: 1999 (contained air) [17]. Open porosity is related to the voids that intercommunicate, allowing the circulation of fluids inside (the material is more or less permeable as a function of the size and geometry of the pores and of the connectivity in the pores' net) [51].

The open porosity of cementitious mortars corresponds to around 20 % of the pores volume, comprising around 75 % of micro-pores (diameter less than 0.1 μm) and 25 % of macro-pores (diameter more than 0.1 μm); mixed-binder mortars fall between cementitious and lime mortars (the latter have the largest pores volume, comprised mostly of macro-pores) [52]; the open porosity of air lime at a 1:2 volumetric proportion varies as a function of the lime slaking time (35 % for quicklime with 10 months of slaking time and 40 % for 16 months slaking time) [47].

Fig. 2.13 (**a**) Capillary absorption test on lime mortar specimens [21]; (**b**) water permeability test [53]

The apparent or open porosity may be measured by intrusion techniques or microscopy. The most current ones are water immersion or mercury porosimetry, the latter also allowing obtaining information on the pore distribution (size and shape of the pores) [53].

Capillarity

Capillarity is the property that a hardened mortar has of absorbing water naturally without pressure exertion [17], measured by the water mass absorbed by capillary forces per area unit of the material. The capillary absorption test consists generally on the periodic measurement of the mass variations of samples over a period of time, positioned with one face in contact with a thin water layer (Fig. 2.13a) and cleaned with a cloth after each weighing. The cyclic procedure of surface cleaning, weighing and repositioning is maintained throughout the test over several measuring periods.

The capillarity coefficient corresponds to the slope of the specimen mass versus time graph at 10 and 90 min and is expressed in kg/m^2 min$^{0.5}$ for the mortars scoped by EN 998-1: 2010, except for renovation mortars, for which this coefficient is expressed in kg/m^2 after 24 h (or when the linear relationship referred to does not exist); the capillarity coefficient (*C*), at 28 days, is determined according to EN 1015-18: 2002, and the standard requirement is summarized in Table 2.7 (the standard does not include mortars whose main binders are calcium sulphate or air lime).

From technical specifications, mostly on pre-dosed renders, it is found that the capillarity coefficient (*C*) has an upper limit of 0.4 kg/m^2 min$^{0.5}$, which may be exceeded in general use mortars (products that usually have a finish layer of another material that provides an additional protection against capillary suction).

The upper limit of 0.4 kg/m^2 min$^{0.5}$ is also recommended for application in damp or cold weather and for sprayed finish. However, a stricter control of capillary absorption must be made under specific conditions, such as [21]:

Table 2.7 Requirements for the performance (water resistance characteristics) according to EN 998-1: 2010

Characteristics	Type of requirement		Requirements					
			GP	LW	CR	OC	*R*	*T*
Capillarity coefficient (C), in kg/m^2 min$^{0.5}$	Classes	Average values	W0–W2	W0–W2	W0–W2	W1–W2	≥ 0.3 kg/m^2 after 24 h	W1
	W0	No demand						
	W1	$C \leq 0.4$						
	W2	$C \leq 0.2$						
Water penetration after capillarity tests (mm)	Measurement after capillarity test		–	–	–	–	≤ 5 mm	–
Water under pressure permeability, after climatic cycles (mL/cm^2 after 48 h)	Value after the test		–	–	–	≤ 1	–	–
Water vapour permeability coefficient (μ)	Value declared by the manufacturer (VD)		$\leq$VD	$\leq$VD	$\leq$VD	$\leq$VD	≤ 5	≤ 15

- Wall exposed to shocks, in locations next to roadways or railways ($C < 0.15$ kg/m^2 min$^{0.5}$)
- Render applied at the bottom of walls (height of 15–30 cm) or in severe in-service conditions ($C < 0.20$ kg/m^2 min$^{0.5}$)
- Strong exposure to rain, medium/high pollution and/or without protection elements against runoffs, very absorbent substrates or those with very weak mechanical strength, façade areas below 3 m or above 18 m and paint finish ($C < 0.25$ kg/m^2 min$^{0.5}$)

Traditional renders, because they do not use water-repellent compounds, have higher capillarity coefficients, even cementitious ones. According to Cahier 1778 from CSTB, hydraulic binder coatings are divided in three categories: strong capillarity ($C > 0.4$ kg/m^2 min$^{0.5}$); weak capillarity (0.15 kg/m^2 min$^{0.5}$ $< C <$ 0.4 kg/m^2 min$^{0.5}$); very weak capillarity ($C < 0.15$ kg/m^2 min$^{0.5}$). For example, studies on hydraulic lime mortars obtained capillary coefficients between 0.90 and 1.58 kg/m^2 min$^{0.5}$ [54], similar to those obtained in air lime mortars with 1:3 volumetric proportion, in the range between 1.14 and 1.58 kg/m^2 min$^{0.5}$, at 28 days [7].

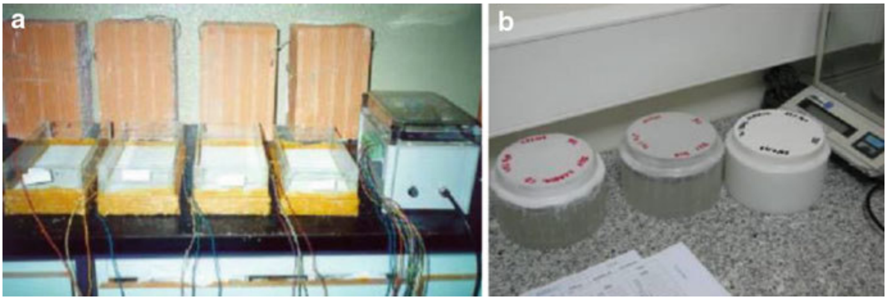


Fig. 2.14 (**a**) Moisture measurement test, drying phase [55]; (**b**) water vapour permeability test [21]

Permeability to Water

Permeability to water is the property of the material being passed by water under a pressure gradient. According to EN 998-1: 2010, the permeability to water under pressure for a period of 48 h under climatic cycles is considered; in this laboratory test (Fig. 2.13b), a height of 10 cm of water is created over each of the specimens and then the amount of water passing through the specimen is measured against time, according to Cahier 2669-4. For standard EN 1015-21: 2002, this measurement is made after accelerated ageing associated to climatic cycles, leading to a requirement for pre-dosed one-coat decorative mortars (Table 2.7), which is also referred in report 427/05 from LNEC for all industrial mortars.

According to Veiga [23], the values obtained using the EN 1015-21: 2002 technique are not directly comparable between multi-coat and one-coat renders, because what is measured is the water absorbed by the material and not the water that reaches the substrate, which may be concentrated almost only in the last coat and therefore not really affect the render's performance, which may remain good because of the effect of the various coats. Therefore, an equipment to measure moisture was developed at LNEC, allowing evaluating the time rainwater takes to reach a substrate and the time it takes to dry afterwards (FE Pa 38: 1999—waterproofing test) (Fig. 2.14a); the parameters evaluated by this technique are wetting delay (M); dampening period (S) and wetting rate (H). Sá [44] shows results using this technique for air lime mortars at 28 days (e.g. an air lime mortar with siliceous sand with 1:3 volumetric proportion with $M = 0.17$ h; $S = 30$ h; $H = 9.24$ mV h × 10^{-3}).

Permeability to Water Vapour

In theory, the level of water vapour permeability demanded from a render grows with its water permeability, so that the ease with which water is released is proportional to the amount that has passed through the coating [20]. The water vapour permeability can be measured, taking into account constant temperature conditions, different vapour pressures in environments with distinct air relative humidity levels and the surface and the thickness of the material [52]. By definition, it is equal to the flux of water vapour that passes through the mortar, under balanced conditions, per unit of surface and vapour pressure [17].

The permeability can be measured by the coefficient of resistance to water vapour diffusion (μ), which is a characteristic value of the materials, obtained by the non-dimensional ratio between the air water vapour permeability and the material's water vapour permeability, and it indicates how many times the resistance to diffusion of a specimen of this material is greater than that of a still air layer of equal thickness and subjected to the same environmental conditions [56]. The current test method resorts to standard models "cup shaped" partially filled with a liquid (Fig. 2.14b); the determination of the coefficient of resistance to water vapour diffusion (μ) is made based on the water vapour permeability (Λ) in kg/(m^2 s Pa), at a temperature of 20 °C and atmospheric pressure of 101,325 Pa (EN 1015-19: 2005); the water vapour permeability can be expressed by the thickness of air layer with a diffusion equivalent to 0.10 m of render (S_d), i.e. $S_\mathrm{d} = \mu * e$, where the thickness e is in metres [45].

In technical specifications it is found that the water vapour diffusion coefficient (μ) can be equal to 5, 15, 20 or 30 for coating mortars, according to EN 1745: 2012 (mortars with density between 200 and 2,000 kg/m^3 and thermal conductivity between 0.07 and 1.28 W/m K); the requirements for this characteristic depend on the value declared by the manufacturer; however, an upper limit is recommended for the water vapour diffusion coefficient ($\mu \leq 15$) (Table 2.7) or the air layer with diffusion equivalent to 0.10 m of render ($S_\mathrm{d} \leq 0.15$ m) for industrial renders (427/05 from LNEC); the current μ values in lime and cement mortars are 15–35 (density between 1,800 and 1,900 kg/m^3) and in cement mortars 15–41 (density between 1,900 and 2,100 kg/m^3) [56]; for mixed-binder and lime mortars the current values are 20 and 10, respectively [52].

2.3.3.9 Chemical Resistance

The mortar's durability depends on its chemical resistance (to the salts and pollutant agents action), and no situations that favour a physical-chemical and consequent biological attack must occur. To guarantee this, various chemical parameters must be studied in non-degraded and degraded specimens, to establish acceptable values for the soluble salts content, the pH value and the conductivity (a fast increasing field of research).

Soluble Salts Content

Efflorescence is a crystalline deposit that takes shape on the surface or in the internal coats of a coating, due to physical-chemical actions made possible by the presence of water, affecting the aspect of the surface but also able to generate chemical and physical degradation (salts crystallization). The most common salts found in efflorescence occurrences are carbonates (from limes and cements), sulphates and chlorides (from ceramics, aggregates and additions, mixing water or brick-cement reactions) and also nitrates from fertilized or contaminated soils [57].

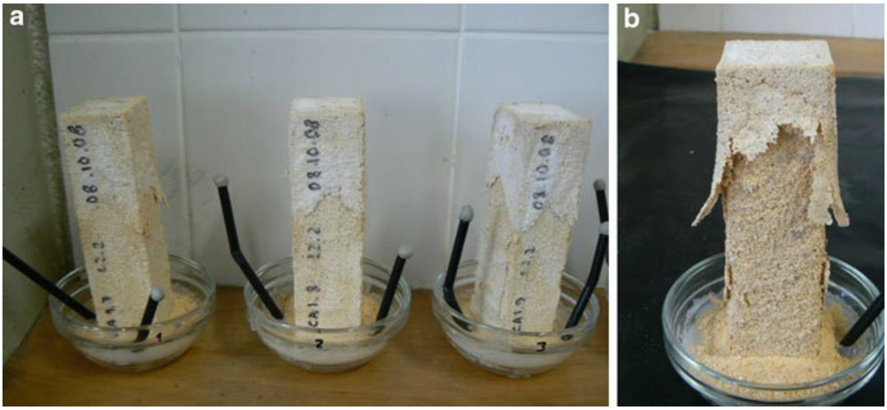


Fig. 2.15 (**a**) Test by contamination of mortars by capillary rise of a solution of sodium chloride at 15 %; (**b**) sample at the end of the test [photos by R. Nogueira]

The simplest methods for salts detection resort to the water solubility these compounds have, to a greater or lesser degree; if there are insoluble compounds (such as calcium or magnesium carbonates, which result from the carbonation of lime lixiviated from the mortar or from non-carbonated lime), other analysis methods are used (based on the chemical reactivity these compounds have with acids). Generally, the laboratory evaluation of the mortars' performance in terms of salts crystallization is made in prismatic specimens that are repeatedly contaminated with saline solutions, usually sodium chloride, and subjected to various drying conditions, which essentially lead to a degradation of the specimens' volume as a whole, with consequent loss of mass (Fig. 2.15); studies refer losses of mass in the sulphates resistance test between 30 and 40 % in air lime mortars with 90 days of curing [47].

Very often the degradation caused by these tests does not come close to the degradation pattern of mortars in service, since the contamination with soluble salts occurs slowly and continuously; the evaporation of saline solutions and the location of the "drying front" may vary, as a function of the environmental conditions and the percolation of the solution, among other factors. On the other hand, the use of more specific laboratory techniques may more reliably characterize the identification of the soluble salts (e.g. sulphates, chlorides and nitrates), the nature of the constituents, the binders percentage, the constituents morphology, the diagnosis of the deterioration processes and the nature of the organic compounds present [55].

There are no performance criteria for the concentration of soluble salts in mortars. Generally, the salts that most contribute to hygroscopicity phenomena are nitrates and chlorides in contents higher than 0.1 % or 0.09 %, respectively, of the weight of the specimen analysed [58]. A Brazilian study of mortars traditionally used in a given region found out that the presence of nitrates was rare, sulphates had contents below 100 g/m^3 of mortar and chlorides occurred with contents around 180 g/m^3 of mortar; after this study, the authors found that chloride and sulphate contents of 100–500 g/m^3 did not change the properties of the mortars in the hardened state [59].

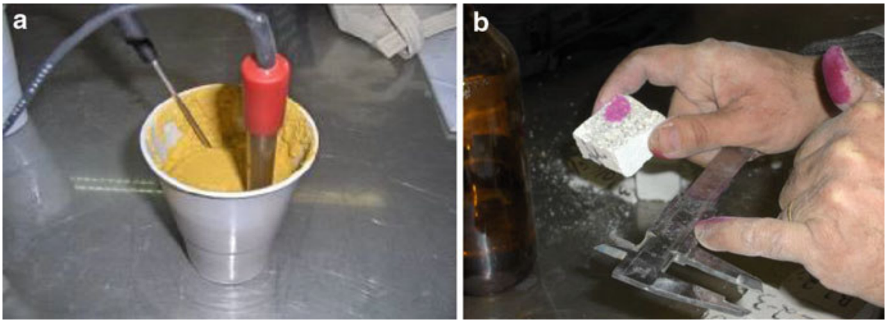


Fig. 2.16 (**a**) Measurement of the pH in a fresh industrial mortar; (**b**) measurement of the carbonation depth of a lime mortar with the help of a calliper, after a phenolphthalein test

pH and Conductivity Values

The determination of the pH and conductivity is made resorting to an electrometric process in a mortar sample (Fig. 2.16a), from the dilution of a small quantity of product resulting from the scraping of a rendered surface; this technique is vastly used in the evaluation of the quality of water ("clean or wastewaters"), soils and lixiviated compounds [21].

The pH of a fresh mortar (cementitious or mixed-binder) mixed with water is around 11–12 because of calcium hydroxide ($Ca(OH)_2$) in its composition; therefore, the pH value can give clues about the mortar's alkalinity at any given moment, if analysed with the percentage of existing calcium hydroxide; alkalinity is the main responsible for the deterioration of the acid pollutants in the atmosphere [52]. The variation of pH may occur in service, e.g. by dropping to values close to 7 by carbonation (absorption of carbon dioxide from the atmosphere) that depends on the porosity and service life (in the case of cement mortars, this may take several years); since this transformation occurs only in the superficial layer in contact with the environment, the pH variation does not provide information on the internal performance of the render system (inner coats' behaviour). The carbonation depth can be determined by spraying the specimen with phenolphthalein (pH indicator: pink in non-carbonated samples with $pH > 10$ and colourless in carbonated samples with pH between 8 and 10) [21] (Fig. 2.16b). On the other hand, the pH analysis may characterize areas prone to biological attack (bacteria thrive at an optimum pH between 4 and 6, while fungi favour the 7–9 range, and most algae develop with a pH of 8).

2.3.3.10 Surface Condition (Finish)

Renders must comply with uniformity and surface flatness requirements; they must not show perceptible surface defects or irregularities, such as localized recesses or protrusions, cracks, swelling, debonding or pulverulence. The surface texture must be regular and uniform [20]. From the requirements collected, it is concluded that [21]:

- A good smoothing capacity of the render can be guaranteed with maximum geometrical deviations of 10 mm, for global planeness, and 2 mm for local planeness (measured with a ruler); the verticality of surfaces must limit vertical deviations to 15 mm (measured with a plumb line 3 m long); these requirements increase when the points and lines application technique is used (5 mm for global planeness and 10 mm for verticality), according to DTU 26.1:1994 (NF P 15-201-1); standard EN 13914-2: 2005 recommends limits for these parameters in interior renders.
- The differences in texture (roughness) of the coating should not be significant, even though there are no specific requirements.
- The colour and glow homogeneity can be controlled when limited to the global difference in colour by coefficient $\Delta E \leq 2 \pm 0.6$ and in gloss by coefficient $\Delta p \leq 5\ \%$ [60].
- The surface must be free of features that may decrease the render's performance, such as cracks (more than 0.2 mm in current areas), detachments and stains. In areas especially designed for concentration of cracks (e.g. joints, grooves), greater widths may be tolerated [20].
- The solar radiation absorption coefficient (α_S) depends on the surface's colour, and it is recommended that it should be below 0.7, conditioning the use of dark colour coatings in exterior surfaces (this may considerably increase the coating's surface temperature, with a consequent greater sensitivity to thermal shocks; the effect of the surface's roughness or of the dirt deposits should not be underestimated) [61].

2.3.3.11 Durability (Service Life)

The durability design of rendering mortars must take into account the following parameters: service life (period of time, in years, after the construction during which the performance requirements are reached or exceeded, under normal use and maintenance); maintenance needs; ease of performance of maintenance actions; resistance to exposure conditions (e.g. climatic actions). Renders require normal maintenance actions, namely cleaning the rendered surface and small repair work in cracked or detached areas; if these actions are performed periodically and when needed, the expected service life of this coating type ranges from 20 to 60 years, with values between 30 and 35 years for cementitious mortars. Additionally, the project tender (including details) must take into account the in-service conditions that may significantly reduce the expected service life, namely in industrial environments, polluted or maritime or substrates with soluble salts.

There are no durability requirements in EN 998-1: 2010, except for the verification of the adherence and of the permeability to water under pressure (EN 1015-21: 2002), after climatic cycles, for one-coat mortars (in these tests the compatibility of the mortar with the substrate is also evaluated and the eventual degradation of the mortar after the climatic cycles is also looked into) (427/05 from LNEC).

2.4 Design and Execution

This section comprises a comparative analysis between renders made on-site (traditional renders) and pre-dosed in a factory (industrial or non-traditional renders), in terms of design, manufacturing technology, preparation and application, constituent layers of the coating system and types of finish. The use of good quality traditional renders implies execution demands hardly compatible with the needs of present working sites; the main constraints of this render type relative to non-traditional renders are the following [12, 16, 18, 20, 21]:

- Qualified workmanship is necessary to choose, use and dose the appropriate materials (sands and binders) and to conveniently prepare the compositions; very often it is difficult to procure various materials (natural limes and sands with well-adapted size distributions); on the other hand, non-traditional renders (premixed products) are subjected to an internal quality control that guarantees uniform quality and the maintenance of the characteristics.
- The ever faster pace demanded from construction leads to non-compliance of execution procedures of traditional renders (execution in unfavourable weather conditions and systematic disrespect of the drying periods and of the number or thickness of the coats); on the other hand, non-traditional renders are formulated in such a way that they can theoretically perform with one coat the functions of a traditional render applied in three coats; if they are pigmented, they can do without paint application (very common in traditional renders); the execution of non-traditional renders is faster, since it consists only on the mixing of a powder with water and most of the times on applying a single coat by mechanical spraying.
- The emergence of new substrate materials with very different mechanical strength and dimensional stability (and others) characteristics, not compatible with traditional renders.
- The space needed at the working site may be significant for traditional products (e.g. materials stocking), and there are other constraints; on the other hand, the use of premixed contributes to the organization of the working site and the rational use of public space; its use is less aggressive to the environment, namely through the reduction of waste; mortars in bags or in bulk (for silos) guarantee stocking demands of around 3 and 6 t/m^2, respectively, values that are unattainable in traditional procedures.

Notwithstanding the previous limitations, traditional renders have some advantages relative to industrial renders. The latter have a much higher initial cost of the material, demand specialized workmanship and a strict planning on-site and very plane masonries; pigmented renders are not painted and therefore require special care after application, namely at the level of work planning, since later repairs significantly affect the final aspect of this coating type. When their technology is imported, these products may have final aspects that do not match the surrounding architecture, and the experience on their use is smaller than for traditional renders (however, its knowledge has been increasing with the growing experience and reliance of the manufacturers on research, as well as the growing application of European standards on requirements, attribution of CE marking and recommendations at the level of design, preparation and application of these products).

2.4.1 Constituent Materials

The term “mortar” corresponds to the mixture of one or more organic or inorganic binders, aggregates, fillers, additions and/or admixtures and water [17]. In this section the categories of constituent materials of rendering mortars are succinctly characterized.

2.4.1.1 Binders

Binders are materials that participate in the hardening reaction of a mortar; they must be selected and dosed in order to minimize the coating’s shrinkage and the modulus of elasticity; binders used in rendering mortars are essentially inorganic: air binders (air lime and gypsum), hydraulic binders (hydraulic lime, cement and blast furnace slag) and other binders (clay soils, natural pozzolans and fly ashes) [62]; the last group includes materials that by themselves do not have a binding function, unless other components that react with water and provide that property are added [63]; a binder has a hydraulic behaviour when, after having reached a stage of hardening, it does not lose it in permanent contact with water; a binder has an aerial behaviour when, after reaching a given hardening degree, it totally or partially loses it when in permanent contact with water. The main types of binder are described [12, 20, 21], differentiated in terms of their use in traditional and non-traditional renders (Table 2.8):

- Cement—it can be Portland normal (CE I), Portland composite (CE II), blast furnace (CE III), pozzolanic (CE IV), white (with similar characteristics to type I Portland, except that it does not contain iron oxides that are the cause of the grey colour) or other types; cements are hydraulic binders made of anhydrous constituents, crystallized or vitreous, essentially composed by silica, alumina, lime and iron oxide (essential constituents of natural raw materials such as limestone and clays); the percentage of the main compounds of cement is approximately 55 % $3CaOSiO_2$ (bicalcium silicate), 20 % $3CaOAl_2O_3$ (tricalcium aluminate), 8 % $4CaOFe_2Al_2O_6$ (tetracalcium ferroaluminate), 12 % $3CaOAl_2O_3$ (tricalcium silicate) and 5 % $CaSO_4{\cdot}2H_2O$ (calcium sulphate, resulting from the incorporation of gypsum to regulate the cement’s hardening rate); to produce cements other constituents may yet be incorporated, such as industrial products (e.g. fly ashes from electric power plants) or natural products (e.g. fillers or pozzolans).
- Hydrated or slaked air lime—it results from the decomposition by heating of limestone with a content no lower than 95 % of calcium carbonate ($CaCO_3$) or

Table 2.8 Constituent materials of traditional and non-traditional renders [21]

Materials	Traditional renders	Non-traditional renders
Cement (in compliance with EN 197-1: 2000)	Portland composite (clinker and fly ash, slag or pozzolans); in some cases other types may be used (Portland normal, Portland white or blast furnace cement)	Portland normal, Portland composite, white cement (due to colour requirements, it includes lower percentages of melting agents, alumina and iron, which forces heating at higher temperatures than grey cement—1,550 °C)
Hydraulic or slaked air lime (in compliance with EN 459-1: 2010)	Used as binder, as a complement of cement	Natural hydraulic lime and/or slaked air lime in powder (binder with low mechanical characteristics and shrinkage that is used mixed with cement or hydraulic lime)
Other binders	Not applicable	Other special mineral binders
Aggregates (in compliance with EN 13139: 2002)	Natural sands extracted from the riverbed or sandpits, of siliceous, calcareous, silica-calcareous or clayish nature; the size distribution must be continuous and well balanced, so that the fine elements content (size from 0 to 0.2 mm) is around 15 %	Sands of the same nature as those used in traditional renders, namely of siliceous and calcareous nature; the criterion of continuous size grading is not as imperative, since the sand's characteristics may be conferred or modified by the incorporation of lightweight fillers or admixtures
Admixtures (in compliance with EN 934-3 + A1: 2012)	Relatively low use, except for water-repellent compounds	Some admixtures act temporarily during application and setting, while others change permanently the product's characteristics. The ones most used are water retainers, plasticizers, adherence-promoting agents, air entrainers (very common), hydrophobic, fungicide agents, among others
Additions	Relatively low use	Small contents of lightweight fillers (expanded polystyrene granules, expanded perlite, expanded vermiculite, expanded glass granules) and in some cases mineral fibres (e.g. glass, cellulose or polyaramid fibres) and natural or artificial pozzolans; use of mineral pigments (EN 12878: 2005)
Water (in compliance with EN 1008: 2002)	Without impurities	Without impurities

calcium and magnesium carbonate (dolomitic limestone); by heating the limestone at around 900 °C, the endothermic reaction of lime calcination occurs with formation of calcium oxide or quicklime (CaO):

$$CaCO_3 + 42.5\ \text{calories} = CaO + CO_2$$

In the reaction of slaking of quicklime (expansive exothermic reaction), by water spraying or immersion, slaked lime in powder or in paste (calcium hydroxide, $Ca(OH)_2$) is obtained. The calcium oxides and hydroxides are basic or alkaline ($pH > 12$) products:

$$CaO + H_2O = Ca(OH)_2 + 15.5\ \text{calories}$$

The hardening of slaked lime occurs by carbonation (exothermic reaction), i.e. reaction of the atmospheric carbon dioxide (CO_2) with the calcium hydroxide leading again to calcium carbonate ($CaCO_3$) and release of water (H_2O); the carbonation process is effective only in humid ambient:

$$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$$

Setting and hardening of lime-based mortars are slow (the concentration of carbon dioxide on air is very low, around 0.03 %), depending on the lime's hydraulicity (linked to the clay content, which is defined by the hydraulicity index that measures the ratio between the amount of oxides within marls' clays and the amount of oxides within the marls' limestone).

- Hydraulic lime—it has medium mechanical characteristics, adequate to most substrates, and is obtained by firing marly limestone (with clay content between 5 and 20 %); it can be natural or artificial; the hydraulic limes available in Portugal are natural, eminently hydraulic with hydraulicity index over 0.42; natural hydraulic limes result from firing clayish limestone rock (with 10–20 % of clay), followed by slaking of the quicklime and pulverization; between 1,200 and 1,500 °C, calcium oxide forms and part of the calcium is combined with silica and alumina, forming silicates and aluminates; these limes have the property of hardening in water and are the more hydraulic the greater the clay content in the raw material; they harden slower than cement, providing a greater plasticity; artificial hydraulic limes, with very distinct characteristics from natural limes, are in fact lean cements obtained by adding filler (generally limestone aggregates) to Portland cement clinker.

2.4.1.2 Aggregates

Aggregates are granular materials that have no intervention in the mortar's hardening reaction: they can be classified as coarse and fines (sands), according to whether they are retained in the 4.75 mm sieve [20]. In rendering mortars, sand is mostly used as aggregate (Table 2.8), even though some types of finish require various percentages of sands of various sizes or even coarse aggregates (e.g. very rough finish demands a small content of aggregates with size above 5 mm).

2.4.1.3 Admixtures

Admixtures are organic or inorganic materials added in small amounts with the objective of modifying the fresh and hardened mortar properties. Most of them may perform simultaneously several functions, and therefore a compromise is needed in terms of the admixtures to be used. Admixtures must not harm the render's strength and durability nor its application and hardening (EN 13914-1: 2005). Out of the admixtures found useful in rendering mortars, the following stand out [12, 18, 20] (Table 2.8):

- Adherence promoters—generally made of resins (polyvinyl acetate, acrylic polymers, styrene-butadiene or latex), they are used to improve the adherence without increasing the cement content; they also increase the tensile and flexural strength, contributing to the reduction of the modulus of elasticity.
- Hydrophobic (water repellent)—generally made of fine insoluble particles (normally metal salts of organic acids in emulsion such as stearates of calcium, zinc, aluminium or magnesium), in contents below 2 % of cement mass, they are used to clog the capillary vases, reducing capillary and improving the mortar's waterproofing capacity.
- Air entrainers—they are generally sodium alkaline salts, soluble in water, of organic compounds (wood resins, lignosulphonate acid, sulphonated hydrocarbons, fatty acids); during mixing, they cause the development of small closed air bubbles, stable, approximately spherical and with diameters around 10 μm to 1 mm, that function as capillarity barrier, improving the mortar's waterproofing capacity, the freeze/thaw resistance and the salts resistance (in particular to sulphates); they allow reducing the mixing water, decreasing the density and modulus of elasticity, improving cracking behaviour; on the other hand, they reduce the tensile and compressive strength and may negatively affect adherence.
- Plasticizers—they are extremely fine powdery products (e.g. colloidal clay, bentonite, fatty lime, ground limestone, colloidal products, polyvinyl acetates or stearates) that cause the dispersion of cement particles in the mortar's aqueous phase, increasing its specific surface and facilitating its hydration; they increase the mortar's workability and decrease segregation, allowing a reduction of the mixing water and eventually the binder content, which results in lower shrinkage; as a side effect, they may retard setting and reduce initial strengths.
- Water retainers—they are generally cellulosic derivatives and may act simultaneously as thickening agents, modifying the rheology of fresh mortar; they limit the risks of premature desiccation of the mortar by water absorption of the substrate and by evaporation in hot weather, making it less sensitive to weather conditions and too absorbent substrates.

- Fungicides—presently, they are made of organic compounds based on nitrogen heterocycles; they stop the settlement of micro-organisms (moulds, mosses and lichens) on the mortar; in painted renders, these admixtures are incorporated in the paint.

2.4.1.4 Additions

Additions are inorganic materials finely divided that can be added to mortars to obtain or improve specific properties. Of the additions considered useful in rendering mortars, the following stand out [12, 18, 20] (Table 2.8):

- Pigments—they are generally metal oxides (iron, chromium, cobalt or manganese oxides or hydroxides) that are added to the mortar in small amounts, lower than 10 % of the binder mass, to confer colour; these additions should not be easily affected by lime, exposure to light or water lixiviation nor have an adverse effect on cement or the remaining mortar constituents (EN 13914-1: 2005).
- Fibres—they are normally alkali-resistant glass fibres or fibrillated polypropylene fibres and sometimes cellulose fibres; they are primarily intended to increase the coating's tensile strength and ductility, improving their cracking resistance, and to increment their shock resistance; they also influence the fresh mortar rheology (thixotropy, consistency) and possibly the hydration and carbonation process; they generally improve the cohesion and water penetration resistance; these constituents should not affect the render's physical and chemical stability.
- Lightweight fillers—they are expanded polystyrene granulates, expanded vermiculite (density between 65 and 350 kg/m^3), expanded perlite (density between 45 and 350 kg/m^3), pumice (density between 300 and 600 kg/m^3) and expanded glass granules; these fillers decrease the coating's modulus of elasticity, its bulk density and its mechanical strength, allowing the manufacture of very deformable renders; they considerably increase the mixing water and shrinkage, which does not necessarily result in an increased cracking susceptibility, namely due to the reduction of modulus of elasticity and increase of ductility; as their main drawback, they reduce the renders' shock perforation resistance.
- Natural and artificial pozzolans—they are silico-aluminous materials that by themselves do not harden under water but when finely divided and in the presence of water react chemically at current temperatures with the free calcium hydroxide of hydrated cement, forming compounds with cementitious properties [15]; they can be natural (some volcanic materials such as some pumices and perlites) or artificial (some industrial subproducts: fly ashes, blast furnace slags, silica fume); these additions improve the resistance to sulphates and silica-aggregates reactions; their incorporation has other favourable effects: it improves the mortar's workability and cohesion and according to some authors it reduces shrinkage; on the other hand there may be negative effects, among which the frequent increase of setting time and especially the delay of hydration and pozzolanic reactions, which may force drying periods longer than those recommended under normal conditions; recent studies have characterized the behaviour of hydraulic limes with artificial pozzolans (metakaolin) in the rehabilitation of ancient buildings [15].

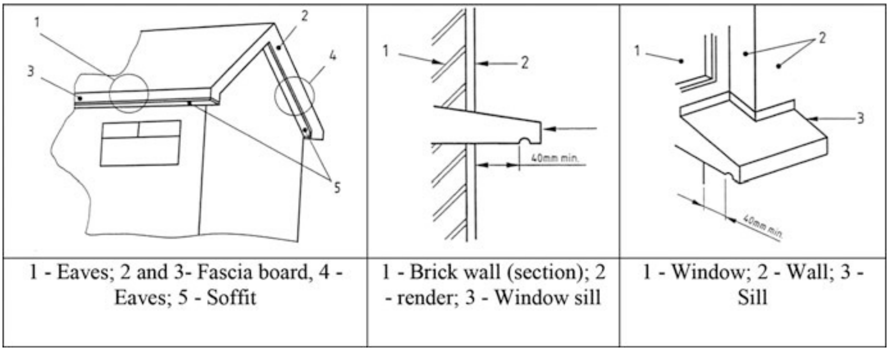
2.4.1.5 Water

Mixing water must be potable and free of impurities (materials in suspension, dissolved salts and organic matter) above a given limit (Table 2.8).

2.4.2 General Aspects of Design and Execution of Rendering Mortars

To use traditional and non-traditional renders, some main design and execution aspects must be taken into account [21]:

- Adequacy of the render to the project (EN 13914-1: 2005), the project must include drawings and specifications with sufficient detail, bearing in mind: the substrate's nature, the render's nature and exposure conditions, the requirements, the render type and the finish type; the influence of embedded metal elements; the influence of architectural details, among others. Some of the aspects referred are described in further detail:
  - The substrate significantly contributes to the render's in-service performance; in this context, its mechanical strength (modulus of elasticity and tensile strength) and water absorption must be compatible with the render applied (including the mechanical, geometric and chemical compatibility between substrate, render and final finish); additionally, the various façade elements must allow admissible tolerances in terms of mechanical, thermal and dynamic actions; in this sense, the design must guarantee the compatibility between the structure and the substrate (partition walls) displacements, as well as the displacements of the masonry blocks and the interfaces with the bedding mortar.
  - The final render finish is another element that can influence the performance requirements of the coating; sprayed finish is the most demanding; however, applying a final paint compatible or a "heavy" coating (e.g. ceramic tiles) leads to a greater demand control; in the first situation, the type of paint must be correctly specified (water based or synthetic; water vapour permeability in the case of membrane-like elastomeric paints); in the second situation, the render's mechanical characteristics are relevant as seen before (category CSIV according to EN 998-1: 2010).
  - Correct building solutions of various wall elements, particularly in what concerns additional water protection (Fig. 2.17), are a crucial factor for a good performance of exterior renders; architectural shapes and drainage devices should evenly protect the façade from the water action, precluding preferential water paths on the surface.
- Reinforcement—to improve the mortars' performance (to support the coating and strengthen specific areas), several types of nets are used: distended metal, with meshes between 15 and 30 mm, protected against corrosion; glass fibres, which must have an anti-alkali treatment to protect from the chemical attack of the mortars [25]; the critical areas are mostly the interface between different



1 - Eaves; 2 and 3- Fascia board, 4 - Eaves; 5 - Soffit

1 - Brick wall (section); 2 - render; 3 - Window sill

1 - Window; 2 - Wall; 3 - Sill

Fig. 2.17 Architectural details relevant for water protection in rendered façades: Eaves and verges (*left*) and window sill with throat minimum dimensions (*centre* and *right*) (EN 13914-1: 2005)

Fig. 2.18 Application sequence of a glass fibre net in the transition zone between a concrete column and a brick masonry wall [64]

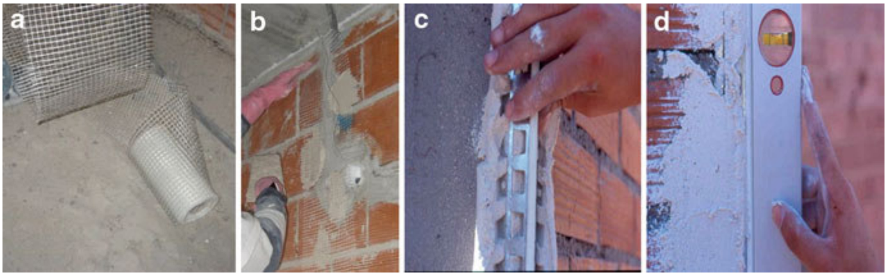


Fig. 2.19 (**a**, **b**) Application of a glass fibre net near filled grooves [65]; (**c**, **d**) execution of corners with a levelled PVC corner profile [64]

materials (Fig. 2.18) and singularities (Fig. 2.19), such as corners of window openings, blinds boxes, sharp edges, coating or structural joints and verges tops; EN 13914-1: 2005 summarizes the reinforcement materials, referring the specifications to prEN 13658-2.

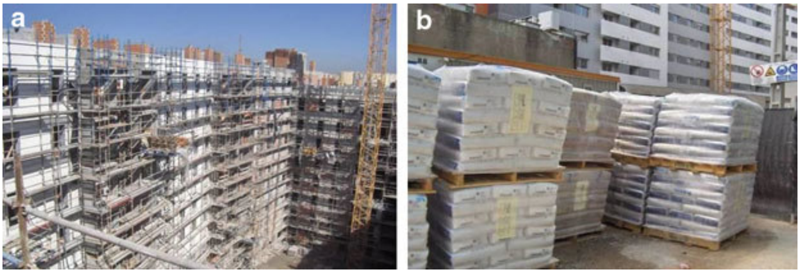


Fig. 2.20 Scaffolding mobilized during the application of exterior renders (*left*) and stocking of pre-dosed products on-site (*right*) [21]

Fig. 2.21 (**a**) Removal of protrusions; (**b**) checking planeness with a ruler; and (**c**) verticality with a plumb line [64]

- Adequacy to on-site local conditions (existing means, regional weather conditions during application, scaffolding (Fig. 2.20a) or other access means, curing times needed, among others).
- Reception of materials (in the case of traditional renders) or industrial products (made in factory), checking all the acceptance criteria (good packing—Fig. 2.20b, and valid term of use).
- Substrate preparation—check its surface regularity, planeness and verticality (Fig. 2.21), surface flatness, cohesion and strength of the substrate, eliminating friable particles in ancient and/or degraded substrates; there must be enough time to inspect the substrate, especially in terms of strength, suction, cleanliness, joints, cracks, dimensional stability, durability (existence of soluble salts or corrosive elements) and adequacy (need of previous treatments, such as application of adherence primer in substrates with bad adherence conditions for render application), EN 13914-1: 2005.
- Application weather conditions—the application of renders must be avoided in unfavourable weather conditions (temperature below 5 °C or over 30 °C, when the wind is strong or when in hot weather the surfaces are exposed to the direct solar radiation) [13]; if the substrate is too hot, it must be previously wetted; on the other hand, render must not be applied on substrates that are saturated with water (e.g. after rainy weather).

2.4.3 Constituent Coats of Renders

Traditional renders must be applied in two or three coats, according to technical recommendations, with different functions and exposure conditions' severity [24]. The need to make these coatings with more than one coat derives from the impossibility of the required characteristics (good workability, good adherence to the substrate, good compacity, low propensity to cracking by shrinkage) being integrally achieved if they are applied with a single coat [20]; another reason is the need to have a thick coating to make an efficient barrier against water penetration. Additionally, cracking that may affect one coat does not necessarily occur in the next one thanks to the discontinuity between coats [20, 62].

According to EN 13914-1: 2005, renders may comprise at least two coats and each one must be weaker than the preceding ones; the number of coats depends on the substrate type, the more or less severe conditions of weather exposure, the type of finish intended and the degree of protection required by the walls; the constituent coats of traditional renders in current façades recommended by Portuguese technical literature are the following [12, 18, 20] (Fig. 2.22a):

- First coat—spatterdash, used to provide good adherence of the coatings to the substrate and reduce/even the substrate's suction; it must be a mortar rich in cement (1:2 volumetric ratio), very fluid (so there is no risk of desiccation of the product by the suction capacity of the substrate and weather conditions), with high content of coarse fillers and applied discontinuously (non-uniform thickness between 3 and 5 mm) and roughly; this coat does not contribute to watertightness and its cracking does not jeopardize the render's task.
- Second coat—smoothing or base coat, whose function is to ensure planeness, verticality and smoothing of the surface and gives the most significant contribution to the watertightness of the wall (low capillarity coefficient, good compacity or admixtures that decrease capillarity, high water vapour permeability), capable of resisting cracking (mortars with low shrinkage and modulus of elasticity); it

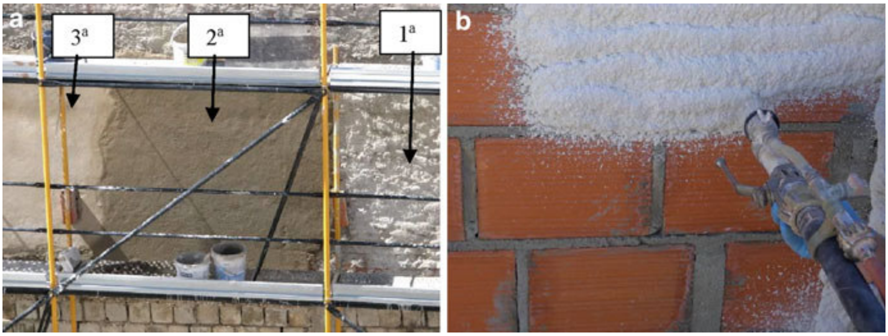


Fig. 2.22 (**a**) Constituent coats of a traditional render; (**b**) application of a single coat of a non-traditional render directly on the brick masonry substrate

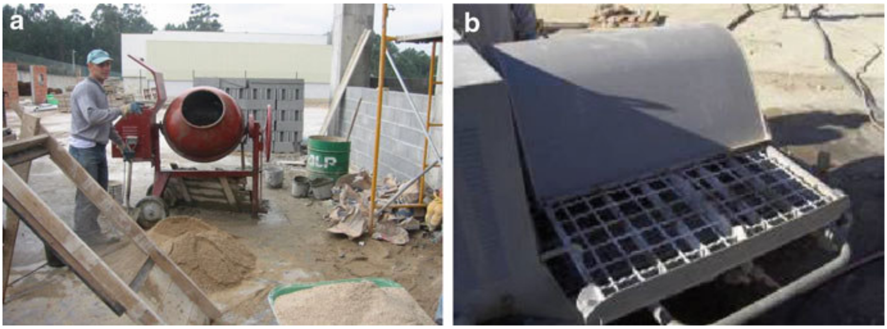


Fig. 2.23 (**a**) Mixing traditional renders in a mixer [64]; (**b**) mixer used to spray premixed mortar [21]

can be applied in a single or a double layer and it should not be more than 20 mm thick; it must be very rich in cement, homogeneous and compact and use sand with a significant content of coarse grains; if in double layer the second one must have less binder than the first one; current volumetric ratios are: 1:1:5 to 6 (cement: air lime: sand); 1:1:6 to 8 (cement: hydraulic lime: sand); 1:3 (hydraulic lime: sand) and 1:5 to 7 + IA (cement: sand + air entrainer).

- Third coat—finishing coat, used to protect the underlying coats and confer the adequate finish (decorative function), because it is directly exposed; this coat also contributes to the wall's watertightness and resistance to shocks and friction, and it must be apt to resist cracking (mortars with low shrinkage and modulus of elasticity); it must be a much weaker mortar (less rich in cement, with a significant content of slaked lime) than the last base coat layer (decreasing cement content from the inside to the outside); current volumetric ratios are: 1:1:6 or 1:2:9 (cement: air lime: sand); 1:1:8 or 1:2:12 (cement: hydraulic lime: sand); 1:4 (hydraulic lime: sand) and 1:6 to 7 + IA (cement: sand + air entrainer).
- Finish—adequate paint system taking into account the physical and chemical characteristics of the substrate made of lime and/or cement mortar, namely alkalinity; water absorption and water vapour permeability; porosity and capillarity; high content of salts soluble in water [66].

The constituent coats of non-traditional renders have the following characteristics [20] (Fig. 2.22b):

- They are almost always applicable in a single coat, often applied in two layers, with total thickness around 15–20 mm; renders with embedded metal net should be applied in two layers and with a minimum thickness of 15 mm, measured from the outer face of the net, according to EN 13914-1: 2005.
- They may require a protection or decorative finishing coat, when their mechanical strength is low or for aesthetical reasons.
- The finishing layers, when pigmented, may guarantee the wall's final finish, with no paint (currently named one-coat pigmented renders).

Table 2.9 Manufacturing and application technology of traditional and non-traditional renders [21]

Operations	Traditional renders	Non-traditional renders
Manufacturing	On-site, dosed according to volumetric ratio prescription, resorting to in most cases to empirical methods to determine the amounts of the materials	In factory, dosed and prepared according to precise and controlled methods
Preparation (mixing)	On-site, with manual preparation, in a mixer (Fig. 2.23a); mechanical mixing improves the homogeneity of the mix and reduces the water content	On-site by adding water to the powder (dry mortars) with mechanical mixes (Fig. 2.23b), maintaining constant the water content (recommended by the manufacturer in the technical file of the product, expressed in litres of water per kg of product), the process and length of the mixing
Application and drying time	Manual or mechanical, with application in three coats, respecting the rule of decreasing binder content so that the stresses transmitted due to shrinkage do not tend to crack the underlying coat and to reduce cracking propensity; each coat must be pressed during application to improve its compacity; waiting period must be sufficient for drying and the greatest part of shrinkage to occur	Manual or mechanical with spraying device, with application of one coat in one or two layers with a waiting period generally between 2 and 5 h, according to the finish type intended Mechanical spraying allows obtaining renders with better characteristics of homogeneity (less susceptible to cracking, more hydrophobic), with various aspects and finish types

2.4.4 Technology of Manufacturing, Preparation and Application

The recent European standard EN 13914-1: 2005 includes technical recommendations concerning the materials and execution procedures; this standard applies to exterior rendering mortars (traditional and industrial) that contain cement, lime or other mineral binders, aggregates, water, admixtures and additions. In Table 2.9 traditional and non-traditional renders are compared in terms of technology of manufacturing, preparation and application.

After preparation, i.e. at the application stage, the sequence of operations differs in these two render types. In the case of traditional renders, it includes [13, 20, 21]:

- Application of spatterdash (3–5 mm)—applied after a significant part of the drying shrinkage of the substrate has occurred, with greater or smaller dampening of the substrate, according to the weather conditions, including cares concerning curing; the mortar must be slapped vigorously against the substrate, manually (in this case using a mason trowel or a float) or mechanically (with a spraying device); the substrate must be thinly covered and the surface must be

Fig. 2.24 (**a**) Points and lines technique for rendering mortars: masonry points in masonry before the application of interior plaster; (**b**) execution of a mortar line; and (**c**) checking its verticality with a bubble level [64]

left rough after spraying; after the application, this coat must be sprayed periodically with water to prevent premature desiccation.

- Execution of points (reference points made of brick pieces bond to the wall with mortar) and lines (filling of a thin strip of mortar, well pressed and aligned, between the reference points) to control the thickness of the base coat (Fig. 2.24) and prepare the singularities (structural joints, verge tops, among others), using reinforcement nets.
- Application of the base coat—under favourable conditions and after a significant part of the drying shrinkage of the spatterdash has occurred (with a time interval of no less than 48 h); previously, the spatterdash must be dampened without causing water runoff; this coat must be slapped vigorously against the substrate, or pressed energetically and uniformly with a float, to improve its compacity; the rugosity needed for the adherence of the following coat must be guaranteed, including checking the thickness of the fresh mortar and the precautions during curing; in the points and lines technique, the space between the lines is filled with mortar, pressed with a trowel or mechanical float, leaving it slightly protruding from the lines and then removing the excess mortar with a ruler supported by the lines. Figure 2.25 illustrates the application of sprayed mortar on substrates with spatterdash, using reference points and a ruler to press, smooth and check the verticality.
- Application of the finishing coat—application under favourable conditions and after a significant part of the drying shrinkage of the base coat has occurred (after 4–7 days after the base coat's application); the finishing coat must comply with the final aspect intended for the surface and the precautions during curing; before the application of this coat, the surface of the coat base must be evenly dampened.
- Application of a final paint coating.

For non-traditional renders, which are pre-dosed in factory and mixed with water on-site (Table 2.9), the following procedures are recommended [16, 21, 68]:

Fig. 2.25 (**a**) Application of the base coat with spraying device, reference points; (**b**) pressing and smoothing/levelling the mortar's coat; (**c**) checking the render's verticality with a reference support [67]

Fig. 2.26 (**a**) Application of one-coat render by spraying; (**b**) pressing and levelling with aluminium ruler; (**c**) final aspect of a mortar joint

- The application of a single coat (20 mm average thickness) is made directly on the substrate (Fig. 2.26a), except when it presents planeness irregularities incompatible with the thickness of the coat; in the case of application in two layers:
  - Application of the first layer—application under favourable weather conditions, with control of thickness and planeness of the fresh mortar by the applier; surface conveniently straightened if a second layer is to be applied or a surface treatment is to be made, complying with all precautions during curing.
  - Application of the second layer—application under favourable weather conditions, a few hours after the application of the first layer; resulting surface perfectly homogeneous and complying with all precautions during curing.
- Pressing and levelling of the fresh mortar—operation made with a wooden, plastic or aluminium ruler (Fig. 2.26b) that is decisive for a good mechanical performance of the mortar (guarantee of a uniform thickness), namely its adherence to the substrate; the mortar must not be smoothed with a trowel so that there is no reflow of the cement laitance to the surface, which would lead to additional shrinkage of that pellicle.

- Points and lines technique—to better control the mortar's thickness and in applications in two layers, the points and lines technique may be used (Fig. 2.24), as for traditional renders.
- Mortar joints—to obtain a uniform aspect of the surface, casting joints must be conveniently located or the mortar must be fractioned; this can be done with wooden or plastic pieces (Fig. 2.26c) with a trapezoidal or half-circle cross section, in order to ease its retrieval after the render hardens, without damaging the edges; alternatively, an adequate cutting tool may be used [64].
- Types of finish—the final finish includes the treatment of the rendered surface and/or the application of a final paint coating; in the first case, the render's drying time and the tools used depend on the type of finish intended [64].

2.4.5 Types of Finish

Textured finishes are preferable to smooth finishes (EN 13914-1: 2005). A very smooth finish is very prone to the development of superficial cracking and the occurrence of water runoff lines, making it difficult to guarantee obtaining a final uniform aspect during execution [12]. A rough finish is more prone to dirt deposits but is more resistant to the establishment of preferential runoff paths in the walls; this finish is also less susceptible to shock and friction actions.

The render's natural colour greatly depends on the type of cement, lime, fine aggregates and mixing water content and can be modified by adding pigments or using a final paint coating; a coloured finish is more prone to cracking due to heat absorption (and consequent increase of thermal movement); colour changes in this type of finish can be greater, namely as white stains, due to the formation of a calcium carbonate skin. EN 13914-1: 2005 divides finishes in several categories, taking into account the surface texture:

- Smooth finish—the surface is finished using fine aggregates, applied with a metal trowel, sometimes after the surface is dry.
- Plain finish—the planeness of the finish depends on the maximum particle size of the sand used; this type of finish requires high specialized workmanship in order to reduce the risk of cracking and irregular discoloration.
- Rough finish—the traces made on the final surface are produced by applying coarser aggregates.
- Textured finish—different textures may be obtained by using different tools and techniques.
- Scraped finish—the texture and pattern are determined by the type of tool used and the type of scraping action.
- Sgraffito—application of acrylic paints with various colours and themes.
- Roughcast—rugosity depends on the shape and size of the coarse aggregate in the mortar mix.
- Dry dash—surface roughness is determined by the size of the pebbles or other stones, cast against the still fresh render coat.

- Sprayed finish—texture depends on the render material used, the type and size of the sprayed particles and the application rate.

Tables 2.10 and 2.11 summarize the most often used finishes in Portugal, respectively, in traditional and non-traditional renders, illustrated in Figs. 2.27, 2.28 and 2.29.

2.5 Pathology and Diagnosis

2.5.1 General Characterization of the Pathology

Out of the current anomalies in renders (with and without paint), cracking, runoffs, detachments, damp stains, dirt, colour changes and biological growth stand out. It is also stressed that the type/occurrence of these anomalies may vary according to the render system applied (traditional, pre-dosed, with paint as finish) [19, 21, 69]:

- In traditional renders (mortars with cement and sand, with two or three coats)—mapped cracking, oriented cracking, cracking of the substrate, loss of adherence (debonding, bulging, detachment), efflorescence and cryptoflorescence, fungi and moulds growth, "ghosts", damp stains and dirt stains; the anomalies of this type of render are caused mainly by the short application deadlines imposed by the works pace (disrespecting drying periods of the masonries and coats) and by inadequate composition and incorrect application.
- In premixed one-coat renders (mortars with cement, sand, admixtures, additions and pigments)—carbonation (surface crystallization of the calcium carbonate salts); stains associated to aspect (colour and texture) heterogeneities, dirt, broken edges (they are mechanically less resistant, despite their greater cracking resistance and waterproofing capacity); the anomalies referred above for traditional renders may also occur.
- Paints—yellowing, bronzing, dirt collection, discoloration, detachment (delamination, peeling or exfoliation), efflorescence, bulging, exudation (diffusion of one or more constituents of the undercoats or the base coat onto the finishing coat), cracking, intumescence (volume increase of the skin due to absorption of a liquid or vapour), stains, stickiness, loss of gloss, loss of coating protection capacity, pulverulence (chalking) and saponification (total or partial dissolution of a paint coating due to the transformation of its fixed vehicle into soluble soaps).

Table 2.10 Types of finishes most current in traditional renders in Portugal [13, 20]

Rough finishes	
Garnishing with a sand mass	Fine texture finish, resulting from light smoothing of the finishing coat using a float or a wooden ruler, eventually wrapped in a cloth to better absorb the cement laitance that occurs on the surface. It may be of two types: (1) "Roscone"—rough fine sanded finish obtained by rubbing a rough cloth over the surface garnished with a sand mass (2) Sponged or sanded—rough finish obtained by rubbing a sponge over the surface garnished with a sand mass
Scraped	Obtained by scraping the whole surface with a toothed blade, a timber board with nails, a timber float lined with a distended metal net or other tool, soon after the mortar starts hardening (2–3 h after execution). Scraping must be done in dry weather and the cement laitance skin must be removed. After scraping, the surface must be scrubbed to remove the loose particles
Polished	Obtained by using abrasives on the whole surface while the mortar hardens (2–8 days after execution)
Scraped and polished	Scraped finish that is then polished with abrasives
Scraped or grooved	Finish obtained in mortars with a small amount of aggregates coarser than the others, which are forced to roll over the hardened base coat using a float, creating grooves as they slip
Rolled	Obtained by pressing the still fresh finishing coat with a roll adapted according to the intended decoration shape
Sprayed	Fine texture finish obtained through mechanical spraying of the mortar over the surface. This finish should have a uniform aspect, and its texture depends on the type of device and mortar used
Sprayed and polished	Finish in which the protrusion peaks resulting from spraying are polished with abrasives. The polishing is made 2–8 days after execution
Sprayed and abated	Finish whose protrusion peaks are abated and smoothed with metal float while the coating is still fresh
Tyrolese	Rough finish, generally markedly so, obtained by manual spraying of the mortar on the surface using a broom. The application must be performed in more than one layer, in order to obtain a marked rugosity. It can be obtained directly by spraying or lightly tapped with a trowel or slightly polished with abrasive, in order to reduce the rugosity
Scottish	Very rough finish obtained through vigorous application on the surface, using a trowel, of a mortar with a great content of coarse aggregates (5 mm $<$ maximum size $<$ 15 mm). The ratio between coarse and normal aggregates should be between 1:1 and 1:2
Dry dash	Very rough finish obtained by casting coarse aggregates on a still fresh mortar coat previously smoothed with a ruler. The aggregates remain exposed and are afterwards lightly tapped with a timber float to better penetrate the mortar. They are usually marble or quartz with maximum size between 5 and 15 mm

(continued)

Table 2.10 (continued)

Washed crushed marble mortar	Coat obtained by applying cement, stone powder and stone granulates (it must be pressed and smoothed but not roughly), with a surface treatment by washing (with a scrub and as little water as possible), while the mortar is still plastic. The natural or artificial aggregates are selected in terms of nature, size grading, colour and shine in order to get the intended decorative effect. The maximum aggregate size is generally between 5 and 15 mm
Smooth finishes	
Floated	Obtained by successive passages with a wooden float on the coat's surface until it is flat and uniform
Polished crushed marble mortar	Washed crushed marble mortar whose surface is polished, manually or mechanically, with an adequate abrasive. The first polish with water is done 3 days after the coating's application, not to loosen the aggregates. After the crushed marble mortar is washed and pores are filled with cement paste with a trowel, the second polish is made with a softer and finer abrasive than the one used initially

Table 2.11 Types of finishes most current in non-traditional renders in Portugal [20, 68]

Rough finishes	
Scraped (Fig. 2.27a, b)	Obtained by scraping the whole surface with a toothed blade, a timber board with nails, a timber float lined with a distended metal net or other tool, soon after the mortar starts hardening (2–3 h after execution). Scraping must be done in dry weather and the cement laitance skin must be removed. After scraping, the surface must be scrubbed to remove the loose particles
Rolled	Obtained by pressing the still fresh finishing coat with a roll adapted according to the intended decoration shape
Sprayed	Fine texture finish obtained through mechanical spraying of the mortar over the surface. This finish should have a uniform aspect thanks to specialized workmanship, and its texture depends on the type of device and mortar used
Sprayed and abated	Finish whose protrusion peaks are abated and smoothed with metal float while the coating is still fresh
Dry dash (Fig. 2.27c)	Very rough finish obtained by casting coarse aggregates on a still fresh mortar coat previously smoothed with a ruler. The aggregates remain exposed and are afterwards lightly tapped with a timber float to better penetrate the mortar. They are usually marble or quartz with maximum size between 5 and 15 mm
Smooth finishes	
Floated or smoothed	Obtained by successive passages with a wooden float on the coat's surface until it is flat and uniform

Fig. 2.27 (**a**) Execution of scraped finish: floating and (**b**) scrubbing; (**c**) application of finish in stone in pre-dosed renders [64]

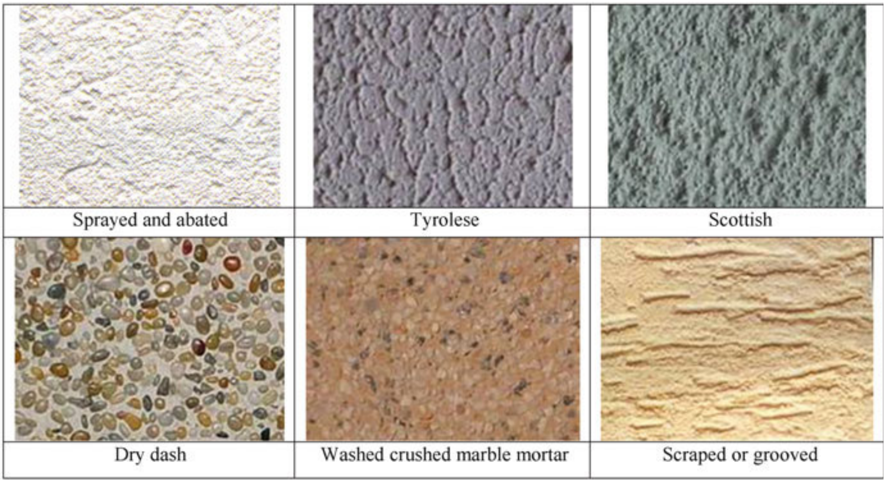


Fig. 2.28 Illustration of some traditional renders finishes

Fig. 2.29 Rugosity of premixed mortar coatings [42]

2.5.2 The Most Common Anomalies in Renders and Their Probable Causes

2.5.2.1 Anomalies Associated with Water

Water is the deterioration agent that most affects construction (it is the primary cause of many anomalies and the secondary one of many others) [70]; humidity leads to the action of other degradation agents, such as pollutant gases dissolved in water, migration of salts dissolved in water; biological growth of organisms in damp environments [26]. The most probable causes may be application of the render before adequate drying of the substrate (construction damp), areas in contact with the soil (ground damp), renders with high water permeability (rainwater damp), hygroscopic salts that draw water in and random causes (rupture of plumbing, downspouts, among others) [19, 21, 26, 30, 70].

2.5.2.2 Cracking and Fissures

Cracking is the most influencing anomaly on the performance of exterior renders (Fig. 2.30), since it affects their waterproofing capacity, seriously harms adherence and, by allowing water/other agents' infiltrations and micro-organisms settlement, reduces the durability of the coating and of the wall itself [26, 42, 70, 71]. A crack is any longitudinal opening that spans the whole render's thickness, breaking it and dividing it into two areas apart; instead, a fissure is a superficial opening, fine and with a discreet development [24, 42]. These anomalies are common in renders and their occurrence is associated to various causes, resulting from the render itself (shrinkage, hygrothermal expansions and contractions, freeze/thaw, deficient content during the mortar's execution, inadequate mortar thickness, excess mixing water) and the substrate, the bond between them (displacements of the substrate, reaction of salts within the substrate, excessive absorption of the substrate) and others (stress concentrations near openings, metal elements corrosion) [19, 21, 70, 71].

2.5.2.3 Efflorescence and Cryptoflorescence

An efflorescence is a saline deposit on the coating's surface, resulting from the migration of soluble salts from the render or the masonry, due to various causes

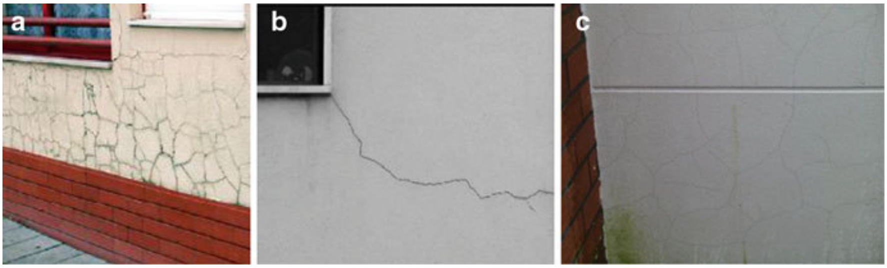


Fig. 2.30 (**a**) Mapped cracking/fissures; (**b**) oriented cracking in traditional render [71]; (**c**) cracking in pre-dosed render [65]

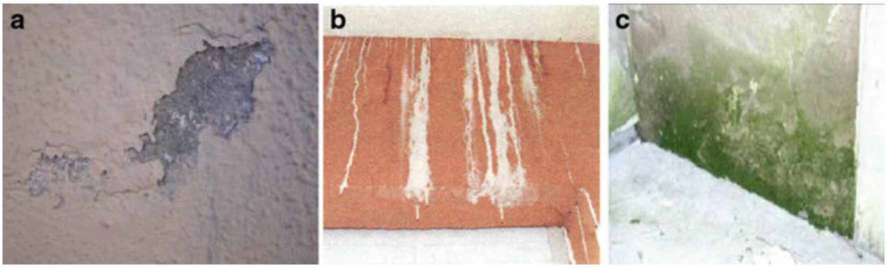


Fig. 2.31 (**a**) Cryptoflorescence in painted traditional render [21]; (**b**) carbonated stains in industrial render [64]; (**c**) settling of algae in traditional render [21]

(prolonged dampening; soluble salts from the render, the substrate or infiltrated water; non-carbonated lime) [19, 21, 26, 70]. They can show up as pulverulent deposits or incrustations, with colour changes on the coating's surface, white, grey, green, yellow or black, according to the salts that give rise to them. Generally efflorescence is just unaesthetic, but its presence may indicate that in another spot crystallization is occurring inside the render's porous structure (cryptoflorescence) (Fig. 2.31a), causing the disaggregation of the surface layer due to the volume increase that is generally associated with salts formation. Sometimes there are other white deposits, non-soluble efflorescence, due to calcium carbonate carbonation, which are told apart for being effervescent in contact with hydrochloric acid [21]; this phenomenon, very common in pre-dosed renders (Fig. 2.31b), is due to unfavourable weather conditions (cold and damp weather) during the render's application, which hinder the combination of free calcium hydroxide [19], or to excessive mixing water.

2.5.2.4 Biodegradation

The presence of organisms or micro-organisms, animal or vegetable (Fig. 2.31c), is harmful to the render, since they deteriorate it, either by their presence, the products they expel or direct attack. Generally, micro-organisms coming from the soil, air or water settle on the coating surfaces, if the conditions are right (prolonged dampening; lack of ventilation/lighting; collection of dust, earth, dirt and pollutants on the rendered surface; high render porosity) [19, 21, 70]. The metabolism products of these organisms progressively attack the render, transforming its surface into a "soil" that allows the germination of plants, which have a mechanical action, namely because of their roots. Finally, an ecosystem is established with the presence of specialized microfauna [72]. The action of small girder animals is also highlighted, such as pigeons that, besides a mechanical action, also attack chemically the render via their excrements [21].

2.5.2.5 Dirt

Surface dirt on renders is very common, since they are exposed to very aggressive conditions. Dust, soot or pollutants settle on the render, making surface deposits

Fig. 2.32 (**a**) Loosening; (**b**) pulverulence; (**c**) erosion [36]

that, even though not attacking mechanically the render, are severely unsightly. The accumulation of dirt is favoured by wind and water transportation, leading to the formation of preferential runoff paths (areas of dirt accumulation in contrast with washing/lixiviation areas). The render's rugosity and porosity are also influential, since they affect the ease of dirt accumulation as well as greater or lesser cleaning difficulty [19, 21, 42, 70].

2.5.2.6 Loss of Adherence

The loss of adherence between render and substrate may be associated to various causes (damp or salts; thermal expansions and contractions; substrate movements; execution errors—excessive mixing water, lack of preparation of the substrate, inadequate mortar composition; substrate's watertightness (liquid or in vapour)) and reveals itself in several manners [36, 70]; the loss of adherence may be characterized by debonding between the render and the substrate, identified as render's bulging/swelling; the render may still completely detach itself from the substrate (Fig. 2.32a).

2.5.2.7 Loss of Cohesion or Disaggregation

Loss of cohesion (Fig. 2.32b) consists on the separation of the render's components, followed by a considerable loss of particles, transforming it into a fragile material prone to degradation [70]. This anomaly is due essentially to the render's low surface hardness that can result from the content or washing of the binder; however, many of the anomalies referred may cause disaggregation, thus being secondary causes of this anomaly (salts crystallization; insufficient render's surface hardness; organism and micro-organisms action; chemical reaction of the render with the natural or artificial materials or environmental pollution) [42].

2.5.2.8 Erosion

Erosion (Fig. 2.32c) results from the action of physical, chemical or mechanical agents on the render's surface, causing its wear and possibly material loss; this type of anomaly may be associated to loss of cohesion referred above, the action of environmental agents (rain, wind, temperature changes) or human agents (shock and friction actions) [36].

2.5.3 Classification of Diagnostic Methods

In situ tests are a precious auxiliary means of visual inspection and allow a better characterization of [73]:

- Degradation mechanisms of the surfaces (e.g. dirt, efflorescence, damp, cracking)
- Properties changes of the render directly related with its performance (e.g. mechanical strength, water absorption coefficient)
- In situ conditions (e.g. environmental parameters)
- Type of materials applied, in conjunction with laboratory tests, on samples collected in situ (e.g. characterization of the mortar's constituents, binder content)

Therefore, performing them allows reducing the subjectivity of visual inspections and more precisely evaluating the effective maintenance needs; it also allows detecting small changes that may be associated to pre-pathology symptoms (modification phenomena prior to the emergence of anomalies that are visible with the naked eye). However, these tests have some constraints, namely increase the inspection time or produce confusing and hard to interpret results, associated to less reliable techniques [73]. The combination of various in situ techniques during visual inspection allows reducing the uncertainty of some of the techniques [21] (Tables 2.12 and 2.13).

The use of more advanced test techniques may significantly improve the collected data and consequently the diagnosis. However, it has another type of limitations, namely the need of specialization of the operator, difficult interpretation of the results and increase of the inspection costs; recent studies identify as advantages of the use of these techniques, offsetting the disadvantages referred, the analysis of the global performance of the façade and the reduced or null intrusion risk [74].

Laboratory tests include tests in specimens, reduced models or real-scale models; they may have two objectives: materials and elements characterization and study of the variation of these characteristics over time through accelerated ageing tests, in particular in elements whose long-term performance is still not characterized. Most of the previous tests resort for practicality reasons to the analysis of specimens and/or reduced models, which makes the analysis of in-service performance difficult (since it significantly depends on the interaction between elements, as in the case of rendered façades).

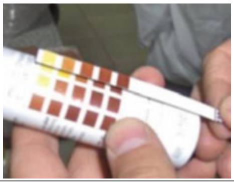
Another experimental method that complements the interpretation of the less intrusive means, such as visual inspection and in situ methods, consists of collecting samples in in-service conditions. This method allows studying the material

Table 2.12 In situ tests for the analysis of in-service mechanical parameters of renders

Test technique/in-service parameters	Technique illustration	Potential on-site
Pull-off resistance to determine the ultimate adherence stress and corresponding type of failure (adhesive or cohesive)		Intrusive technique that allows "probing" the system applied; the analysis of the ultimate stresses of the mostly cohesive failures provides data on the compressive strength (≈10 × failure stress); after the test the samples can be tested for other parameters
Surface resistance using the Martinet Baronnie device that measures the dent diameter and the grid index, associated to impact tests of hard bodies		Characterization of the surface resistance (surface deformability in the 3J sphere impact test) and of the internal resistance (grid test up to 6J) of the mortar applied; evaluation of the depth of the pulverulence-related anomalies
Surface "hardness" given by the pendulum hammer that provides the pendulum hammer index; impact energy of 0.88J for types P, PT and PM sclerometers, but with different impact bodies		Technique with low intrusion degree, allowing mapping with swift detection of poor performance areas (e.g. bulged or detached areas); indirect measure of the compressive strength of the product; need to evaluate the contribution of the substrate to results obtained on-site
Ultrasounds (indirect method) that measure the transition time of ultrasonic waves, allowing the determination of their apparent velocity		It evaluates the internal heterogeneities of the mortar applied; it allows establishing a relationship between the decrease of velocity measured in areas visually sound and those with anomalies (very sensitive to cracking); sensitive to damp on the surface

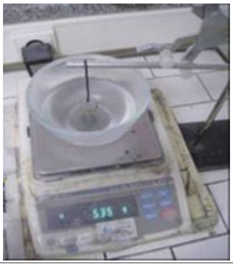
effectively applied and not the one produced in laboratory (under controlled conditions very different from real ones) and also obtaining information on the characteristics that are not evaluated by other verification methods (Table 2.14); another advantage of collecting samples is the calibration of some of the in situ techniques through the correlation between their results in samples collected and in specimens produced in laboratory; despite the advantages referred, samples collection has some limitation due mostly to their intrusive nature. The choice of the tests to be performed on the collected samples and the number of samples depend on the type of analysis and on the technical and economic resources needed.

Table 2.13 In situ tests for the analysis of in-service physical-chemical parameters of renders

Test technique/in-service parameters	Technique illustration	Potential on-site
Karsten tube that measures the absorption of water under pressure for 60 min, in a crack-free area; it allows analysing the water permeability, through an absorption coefficient for a given period of time		Non-destructive technique that allows differentiating products with and without hydrophobic compound; it complements the results of capillarity tests on ion samples; it tells apart several types of finishes
Moisture measurement device that, by the electric impedance principle, measures the percentile moisture content on the surface (scale calibrated with a reference mortar within the device)		Non-destructive technique that allows swift mapping and the diagnosis of the source and/or evolution of moisture spots; sensitive to hygroscopic salts
Infrared radiation pyrometer that measures the surface temperature without contact, allowing calibrating the results for emissivity and ambient temperature values		Non-destructive technique that may allow small mappings of surface temperature; 24 h measurements needed for the analysis of surface condensations
Field kit that measures the concentration of various salts, in mg/L (chlorides, nitrates and sulphates), through the analysis of 2 g of a sample diluted in water + reagents, with a spectrophotometer		It allows evaluating the source of efflorescence and the corresponding concentration of a given salt; it shows some uncertainty in the analysis of sulphates; it requires collecting a powder sample
Colorimetric tapes that measure the concentration of various salts diluted in water, through a given comparison scale (e.g. chlorides: 0–500–1,000–1,500–2,000–3,000 mg/L)		They provide concentration ranges for each ion, which may be useful to rapidly detect high contents of a given salt; there is uncertainty in the limits of each reading range

In recent buildings, the collection of samples has not been a common practice, basically due to its destructive effect on the surfaces, cost and time spent in the analyses; in one-coat renders without a finish coat, the subsequent repair of the sites intervened almost always affects the look of the rendered surface. For these reasons, even when samples are collected it is difficult to guarantee the representativeness of the results because of the significant number of samples that would be needed [21]. In this context, it is the combination of the visual inspection with the in situ techniques that allows choosing the location, number and size of the samples to be collected.

Table 2.14 Laboratory tests for the analysis of in-service of renders

Test technique/in-service parameters	Technique illustration	Potential on-site
Compression test of samples collected directly from the surfaces or that resulted from the pull-off test; measurement of the compressive strength of the product applied		Destructive technique that evaluates the mechanical performance of the render applied; the results may be influenced by the irregularity, degradation and thickness of the sample collected
Hydrostatic weighing test that allows determining the apparent density and the open porosity in small collected samples; it does not allow the analysis of the porometry (pore distribution)		It allows a first mechanical and physical characterization of the render applied; the open porosity may tell premixed products (more porous) apart from traditional ones
Drying test that allows the determination of the drying index, in collected samples (variation of the water content, in percentage, during evaporation, relative to the water content at the start of the drying phase)		Test still at the research stage but that may be an indirect way to evaluate the water vapour diffusion resistance
Capillarity test in samples that measures the capillarity coefficient (through the difference in mass in the time that the test lasts, translated by the graph's slope)		It allows evaluating the applied render's water performance; in the analysis of the results, the thickness of the sample and whether it was saturated during the test must be taken into account
Combined measuring device to determine the pH and conductivity (μS/cm) of a sample diluted in water, through an electrometric process		It provides relevant information for the characterization of the render applied, in a given instance (e.g. identification of the carbonated or chemically attacked areas)

2.6 Maintenance and Rehabilitation

2.6.1 Maintenance Strategies

The ageing process of renders is inevitable. However, the rate associated to the degradation process can be controlled by periodic maintenance actions that may prolong the service life of the façade elements, preventing failures and associated problems. Proactive maintenance of exterior renders allows an adequate monitoring during service life, through the following main means: (a) periodic inspections; (b) interventions on the surface (to guarantee its look)—cleaning, painting or repainting and protection techniques (hydrophobic protection); (c) "light" interventions—repair and local replacement; (d) "heavy" interventions—large repair or replacement.

Periodic inspections during the use stage (predictive maintenance) increase the capacity to detect ("when" and "where") the need for interventions, minimizing the number of unpredicted anomalies (and allowing a growing knowledge of the render's in-service performance, its expected service life and of premature degradation agents); these inspections' objective is to check the emergence of anomalies and the in-service performance, especially in the most severe exposure conditions (risk areas) or after interventions; they may also aim at examining eventual dysfunctions and the actual ageing of all the elements [21].

The in-service performance of façade coatings comprises three main stages: (1) initial, including the first years after construction and characterized by the eventual emergence of premature anomalies (e.g. due to gross mistakes of design or execution); (2) intermediate, whose development depends on various in-service factors and on their influence on the natural ageing of the renders applied; (3) terminal, including the last years of the life cycle, with greater probability of reaching failure. In this context, the planning of actions in rendered walls must include detailed inspections at the initial and terminal stages and current and/or detailed inspections at the intermediate stage of the life cycle.

2.6.2 Classification of the Maintenance/Repair Techniques

To maintain maintenance costs within acceptable limits, the façade and the building must comply with given requirements: easy to maintain; accessible to perform periodic maintenance actions; easy to repair and replace elements. These actions must not in any case modify the aspect of the surface with unwanted effects (gloss, change of colour). The importance of adequate cleaning is stressed, bearing in mind the various causes of symptoms; e.g. the removal of white stains resorting to dry scrubbing, after the surface dries, is efficient in the case of efflorescence (water-soluble salts crystallization on the surface); however, in carbonation phenomena (white stains due to the formation of calcium carbonate, insoluble in water), cleaning normally includes the application of a treatment with diluted acid [21]. Finally, no treatments last forever and therefore periodic inspections and permanent maintenance care are needed; these periodic interventions can control the actual efficiency of the treatments.

The maintenance actions in rendered façades can be divided according to four basic principles: performance monitoring through inspections; change the surface by cleaning and painting operations; mechanical and physical-chemical resistance of the render through local repair/replacement; protection against given agents, particularly water action, by for example applying a hydrophobic product [21]. The option of repairing and replacing the render applied must be equated in the in-service diagnosis, and the final decision depends on safety and the balance between costs and practical considerations. According to BRE GBG 23: 1995, repair is the right option if (1) the adherent render is in a good state or is difficult to remove without affecting the substrate's wall; (2) the cause of the failure is confined to a small area; (3) larger scale replacement works are scheduled for the next 2 years; (4) the impact on the aspect can be minimized by repairing the render in well-confined areas (e.g. panels between windows). The option of replacement is recommended if (1) the state of the render may lead to lack of safety situations; (2) there is an extensive detached area; (3) the defect is evolutionary; (4) the replacement cost is not significantly higher than the repair cost; (5) it is necessary to assemble scaffolding; (6) aspect is very important; (7) the existing render is not the most adequate for the in-service exposure conditions.

2.6.3 Interventions in Renders of Ancient Buildings

Ancient renders are multi-coat systems, comprising smoothing and protection coats (spatterdash, base coat and finishing coat), made of mortars with lime and sand (volumetric proportions 1:1 to 1:5, air lime: sand), with mineral and organic additions (brick powder, natural pozzolans, dolomitic lime, natural fibres, various additions), applied in various layers (from the interior to the exterior the aggregates' size decreases and the deformability and porosity of the layers increase) [75]. Given the diversity of these renders' characteristics, intervention strategies must follow the next steps:

- Know the existing renders through the various diagnosis techniques available for analysis (observation, stratigraphy, chemical, mineralogical and microstructural analysis techniques, in situ and laboratory tests).
- Select the strategy to be used, taking into account the building's conservation state (anomalies' severity), the historical authenticity of the existing materials and the availability of resources to perform the intervention:
  - First option—conservation of the old coating (preventive maintenance and/or local fissures, gaps and finishes repair operations).
  - Second option—consolidation of the existing coating through the recovery of its adherence and cohesion.
  - If the previous options are not viable, consider partial replacement and, only as a last resort, proceed to total replacement.

Table 2.15 Requirements for replacement mortars of exterior, interior and joints repointing renders, in ancient buildings [75]

Mechanical characteristics	Flexural strength	Compressive strength	Modulus of elasticity	Adherence to the substrate	Performance against stresses due to restricted shrinkage
	Similar to those of the original mortars and lower than those of the substrate			Pull-off resistance lower than the substrate's tensile strength: failure must never be cohesive in the substrate	Maximum stress due to restricted shrinkage lower than the substrate's tensile strength
Water-related performance	Water vapour permeability			Capillarity coefficient	Porosity/ porosimetry
	Similar to those of the original mortars and higher than those of the substrate				Similar to that of the original mortars and with greater percentage of large pores than the substrate
Salts-related performance	Salts contents—low				
Thermal performance	Thermal expansion coefficient and thermal conductivity similar to those of the original mortars and of the substrate				
Durability	Resistance against weather actions and salts—medium to high				

For repair or partial or total replacement, materials and techniques compatible with the existing elements must be used, complying with requirements of functional compatibility (not contribute to degrade existing renders, protect the walls, be durable and contribute to the system's durability) and of aspect (not jeopardize the visual aspect, not mischaracterize the building and not suffer differentiated ageing). Table 2.15 presents the requirements for replacement mortars in ancient buildings [75], taking into account the chemical, physical and mechanical compatibility between existing materials and those applied in new interventions [14].

2.7 Standardization

Mineral binders coating mortars are the object of harmonized European standard EN 998-1: 2010, which indicates the code requirements needed for CE marking (in force since February 1, 2005 for the industrial wall coating mortars market, with system 4), and standard EN 13914: 2005, which gives recommendations on aspects related with design, preparation and application of exterior and interior rendering mortars. However, these European standards have a generalist nature at the level of specifications and recommendations. For that reason, complementary national documents are still being used in the European Union countries; even though these countries are no longer in force as standards, they provide many relevant indications concerning this type of coating, sometimes with a larger and more restrictive set of requirements/recommendations than the European standards referred.

In Portugal, the documents with complementary characteristics (additional requirements) are emitted by LNEC or products certification organisms, when the objective is the marking as certified product. The first ones, called “homologation documents”, were supported by Article 17 of RGEU, which stated that these documents were compulsory for non-traditional products; when the Community directive DPC came into force and CE marking became compulsory, these documents became optional and gained a new designation “application documents” (even though RGEU is still in force, its revision (RGE) is at the approval stage). The application documents for pre-dosed mineral binder cement-based coatings are intended to testify the adequacy to use of this coating type and include the criteria and requirements established within CE marking by EN 998-1:2010 and, on the other hand, the additional requirements that LNEC considers relevant for good global performance of exterior coatings, bearing in mind their functions (report 427/05: 2005).

Out of the French technical documentation, technical Cahiers 2669, from CSTB (Centre Scientifique et Technique du Bâtiment) is referred, with technical specifications and test methods for industrial mortars (in May 1, 2004 there were 144 industrial mortars certified by the MERUC classification); the DTU 26.1 (Document Technique Unifié) document defines the general and special technical conditions for the specification, execution and application of traditional renders.

Tables 2.16 and 2.17 summarize the American and European standards relative to rendering mortars.

Books/Magazines/Journals

- 524R-08 Guide to Portland Cement-Based Plaster—ACI Committee 524, 2008, 40p
- ACI Materials
- Cement and Concrete Composites
- Construction and Building Materials
- Journal of Performance Constructed Facilities
- Journal of Fire Sciences
- Journal of the American Ceramic Society
- Cement and Concrete Research
- Materials and Design

Table 2.16 ASTM standards related with renders/plasters and cement-based products

Standard	Year	Title
A641/641M	2009	Specification for zinc-coated (galvanized) carbon steel wire
A653/A653M	2011	Specification for steel sheet, zinc-coated (galvanized) or zinc-iron alloy-coated (galvannealed) by the hot-dip process
B69	2013	Specification for rolled zinc
B221	2013	Specification for aluminium and aluminium-alloy extruded bars, rods, wire, profiles, and tubes
C11	2013	Terminology relating to gypsum and related building materials and systems
C25	2011	Test methods for chemical analysis of limestone, quicklime, and hydrated lime
C29/C29M	2009	Test method for bulk density (unit weight) and voids in aggregate
C35	2009	Specification for inorganic aggregates for use in gypsum plaster
C87	2010	Test method for effect of organic impurities in fine aggregate on strength
C88	2013	Test method for soundness of aggregates by use of sodium sulphate or magnesium sulphate
C91/91M	2012	Specification for masonry cement
C109/109M	2013	Test method for compressive strength of Hydraulic Cement Mortars (using 2-in. or [50-mm] cube specimens)
C123/123M	2012	Test method for lightweight particles in aggregate
C117	2013	Test method for materials finer than 75-m (No. 200) sieve in mineral aggregates by washing
C127	2012	Test method for density, relative density (specific gravity), and absorption of coarse aggregate
C128	2012	Test method for density, relative density (specific gravity), and absorption of fine aggregate
C136	2006	Test method for sieve analysis of fine and coarse aggregates
C142	2010	Test method for clay lumps and friable particles in aggregates
C150/150M	2012	Specification for Portland cement
C185	2008	Test method for air content of hydraulic cement mortar
C206	2009	Specification for finishing hydrated lime
C207	2011	Specification for hydrated lime for masonry purposes
C219	2013	Terminology relating to hydraulic cement
C230/C230M	2013	Specification for flow table for use in tests of hydraulic cement
C260	2010	Specification for air-entraining admixtures for concrete
C305	2013	Practice for mechanical mixing of hydraulic cement pastes and mortars of plastic consistency
C595/595M	2013	Specification for blended hydraulic cements
C631	2009	Specification for bonding compounds for interior plastering
C670	2013	Practice for preparing precision and bias statements for test methods for construction materials
C778	2013	Specification for sand
C841	2013	Specification for installation of interior lathing and furring
C847	2012	Specification for metal lath

(continued)

Table 2.16 (continued)

Standard	Year	Title
C897	2009	Specification for aggregate for job-mixed Portland cement-based plasters
C926	2012	Specification for application of Portland cement-based plaster
C932	2013	Specification for surface-Applied Bonding Compounds for Exterior plastering
C933	2013	Specification for welded wire lath
C1032	2011	Specification for woven wire plaster base
C1063	2012	Specification for installation of lathing and furring to receive interior and exterior Portland cement-based plaster
C1328/ 1328M	2012	Specification for plastic (stucco) cement
C1437	2013	Test method for flow of hydraulic cement mortar
C1438	2013	Test methods for evaluating latex and powder polymer modifiers for use in hydraulic cement concrete and mortar
C1506	2009	Test method for water retention of hydraulic cement-based mortars and plasters
C1764	2012	Test methods for non-metallic plaster bases (lath) used with Portland cement based plaster in vertical wall applications
D75	2009	Practice for sampling aggregates
D1193	2011	Specification for reagent water
D1784	2011	Specification for rigid poly(vinyl chloride) (PVC) compounds and chlorinated poly(vinyl chloride) (CPVC) compounds
D2013	2012	Practice for preparing coal samples for analysis
E84	2013	Test method for surface burning characteristics of building materials
E90	2009	Test method for laboratory measurement of airborne sound transmission loss of building partitions and elements
E96/E96M	2012	Test methods for water vapour transmission of materials
E119	2012	Test methods for fire tests of building construction and materials
E337	2007	Test method for measuring humidity with a psychrometer (the measurement of wet- and dry-bulb temperatures)
E492	2009	Test method for laboratory measurement of impact sound transmission through floor-ceiling assemblies using the tapping machine
E1671	2012	Classification for serviceability of an office facility for cleanliness
E1700	2013	Classification for serviceability of an office facility for structure and building envelope
E2136	2013	Guide for specifying and evaluating performance of single family attached and detached dwellings-durability

- Minerals Engineering
- Materials Structures
- Journal of Environmental Management
- Energy and Buildings

Table 2.17 European standards applied to rendering mortars

Standard	Year	Title
EN 196-1	2005	Methods of testing cement. Part 1: Determination of strength
EN 196-2	2013	Methods of testing cement. Part 2: Chemical analysis of cement
EN 196-3 + A1	2005; 2008	Methods of testing cement. Part 3: Determination of setting times and soundness
EN 197-1	2011	Cement. Part 1: Composition, specifications and conformity criteria for common cements
EN 459-1	2010	Building lime. Definitions, specifications and conformity criteria
EN 459-2	2010	Lime for construction. Part 2: Test methods
EN 459-3	2010	Lime for construction. Part 3: Evaluation of conformity
EN 934-1	2008	Admixtures for concrete, mortar and grout—Part 1: Common requirements
EN 934-3 + A1	2009; 2012	Admixtures for concrete, mortar and grout—Part 3: Admixtures for masonry mortar—Definitions, requirements, conformity and marking and labelling
EN 934-6 + A1	2005; 2006	Admixtures for concrete, mortar and grout—Part 6: Sampling, conformity control and evaluation of conformity
EN 998-1	2010	Specification for mortar for masonry. Part 1: Rendering and plastering mortar
EN 998-2	2010	Specification for mortar for masonry. Part 2: Masonry mortar
EN 1015-1 + A1	1998; 2006	Methods of test for mortar for masonry. Part 1: Determination of particle size distribution (by sieve analysis)
EN 1015-2 + A1	1998; 2006	Methods of test for mortar for masonry. Part 2: Bulk sampling of mortars and preparation of test mortars
EN 1015-3 + A1	1999; 2004	Methods of test for mortar for masonry. Part 3: Determination of consistence of fresh mortar (by flow table)
EN 1015-4 + A1	1998; 2006	Methods of test for mortar for masonry. Part 4: Determination of consistence of fresh mortar (by Plunger penetration)
EN 1015-6	1998	Methods of test for mortar for masonry. Part 6: Determination of bulk density of fresh mortar
EN 1015-7	1998	Methods of test for mortar for masonry. Part 7: Determination of air content of fresh mortar
EN 1015-8	1999	Methods of test for mortar for masonry. Part 8: Determination of water retentivity of fresh mortar
EN 1015-9 + A1	1999; 2006	Methods of test for mortar for masonry. Part 9: Determination of workable life and correction time of fresh mortar
EN 1015-10 + A1	1999; 2006	Methods of test for mortar for masonry. Part 10: Determination of dry bulk density of hardened mortar
EN 1015-11 + A1	1999; 2006	Methods of test for mortar for masonry. Part 11: Determination of flexural and compressive strength of hardened mortar
EN 1015-12	2000	Methods of test for mortar for masonry. Part 12: Determination of adhesive strength of hardened rendering and plastering mortars on substrates
prEN 1015-13	1993	Methods of test for mortar for masonry. Part 13: Determination of dimensional stability of hardened mortars
EN 1015-17 + A1	2000	Methods of test for mortar for masonry. Part 17: Determination of water-soluble chloride content of fresh mortars

(continued)

Table 2.17 (continued)

Standard	Year	Title
EN 1015-18	2002	Methods of test for mortar for masonry. Part 18: Determination of water-absorption coefficient due to capillary action of hardened mortar
EN 1015-19 + A1	1998; 2004	Methods of test for mortar for masonry. Part 19: Determination of water vapour permeability of hardened rendering and plastering mortars
EN 1015-21	2002	Methods of test for mortar for masonry. Part 21: Determination of the comparability of one-coat rendering mortars with substrates
EN 1008	2002	Mixing water for concrete. Specification for sampling, testing and assessing the suitability of water, including water recovered from processes in the concrete industry, as mixing water for concrete
EN 1745	2012	Masonries and masonry elements. Methods for the determination of design thermal values
EN 13055-1 + A1	2002; 2004	Lightweight aggregates. Part 1: Lightweight aggregates for concrete, mortars and injection grouts
EN 13139	2013	Aggregates for mortars
EN 13501-1 + A1	2007; 2009	Fire classification of construction products and building elements. Part 1: Classification using test data from reaction to fire tests
EN 13658-1:	2005	Metal lath and beads—Definitions, requirements and test methods—Part 1: Internal plastering
EN 13658-2	2005	Metal lath and beads. Definitions, requirements and test methods. External rendering
EN 13914-1	2005	Design, preparation and application of external rendering and internal plastering. External rendering
EN 13914-2	2005	Design, preparation and application of external rendering and internal plastering. Part 2: Design considerations and essential principles for internal plastering
EN ISO 7783	2011	Paints and varnishes—Determination of water-vapour transmission properties—Cup method (ISO 7783:2011)

Associations/Organizations/Societies

- European Mortar Industry Organisation—http://www.euromortar.com/home/
- American Institute of Building Design—http://www.aibd.org/
- Portland Cement Association—http://www.cement.org/index.asp
- Cement Kiln Recycling Coalition—http://www.ckrc.org/
- Brick Industry Association—http://www.gobrick.com/
- Council for Masonry Research—http://www.masonryresearch.org
- Expanded Shale, Clay and Slate Institute—http://www.escsi.org/Default.aspx
- Federacion Interamericana del Cemento—http://www.ficem.org/
- Mason Contractors Association of America—http://www.masoncontractors.org/
- National Stone, Sand and Gravel Association—http://www.nssga.org/
- The Masonry Society—http://www.masonrysociety.org/
- Mortar Industry Association—www.mortar.org.uk

- International Masonry Institute (IMI)—http://www.imiweb.org/about/index.php
- International Masonry Society—www.masonry.org.uk
- Brick Development Association—www.brick.org.uk

References

1. Malinowski R (1982) Ancient mortars and concretes: aspects of their durability. In: Histoire of technology, 7th annual volume, Mansell, UK, pp 89–101
2. Nero JG (2001) The evolution in the use and knowledge of the construction materials (part I). From antiquity to the industrial revolution (in Portuguese). Arquitectura e Vida 11:68–73
3. Vitruvius (2006). Architecture treaty (in Portuguese) [Transl from Latin by M. Justino Maciel]. IST Press, Lisbon.
4. Adam JP (1989) La construction romaine. In: Matériaux et Techniques (2éme édn). Grand Manuel Picard, Paris
5. Velosa A (2007) Characterisation of roman mortars from Conímbriga with respect to their repair. Mater Charact 58:1208–1216
6. Santos Silva A, Ricardo JM, Salta M, Adriano P, Mirão J, Candeias A, Macias S (2004) Characterization of Roman Mortars from the Historical Town of Mértola. In: Project CATHEDRAL POCI/HEC/57915/2004, Lisbon
7. Margalha MG (2010) Air mineral binders. Slaking processes and the time factor in their quality (in Portuguese). PhD Thesis in Civil Engineering, Instituto Superior Técnico, Lisbon, 426p
8. Mateus JCM (2000) Traditional principles and techniques for masonry construction in the technical literature between 1750 and 1900 (in Portuguese). PhD Thesis in Civil Engineering, Instituto Superior Técnico, Lisbon, 720p
9. Nero JMG (2001) The evolution in the use and knowledge of the construction materials (part II)—from the Industrial Revolution to World War II (in Portuguese). Arquitectura e Vida 20:68–72
10. Botelho P (2003) Traditional mortars on ancient masonry substrates: Performance in terms of adherence and durability (in Portuguese). MSc Dissertation in Construction, Instituto Superior Técnico, Lisbon, 183p
11. Paulo R (2006) Characterization of traditional mortars (in Portuguese). MSc Dissertation in Environmental management, Materials and Waste Valorisation, Aveiro University, Aveiro, 189p
12. Rodrigues MP (1993) Waterproofing mineral binder wall coatings—experimental modelling of mortars applied on a substrate (in Portuguese). MSc Dissertation in Construction, Instituto Superior Técnico, Lisbon, 278p
13. Ribeiro JP, Bezelga A (1996) Traditional renders. Chapter 11—Wall coatings (in Portuguese). Construction General Processes course bibliography, Instituto Superior Técnico, Lisbon
14. Veiga MR, Carvalho F (2002) Rendering mortars for ancient buildings walls; requirements and characteristics to be complied with (in Portuguese). Cadernos de Edifícios 2:39–56
15. Velosa A (2006) Lime and pozzolans mortars for ancient wall coatings (in Portuguese). PhD Thesis in Civil Engineering, Aveiro University, Aveiro, 250p
16. http://www.apfac.pt. Accessed February 2010
17. EMOdico (2001) Technical dictionary. European Mortar Industry Organization, Brussels
18. Veiga MR (2001) Performance of wall coatings: Contribution to the study of their cracking resistance (in Portuguese). PhD Thesis in Civil Engineering, Faculty of Engineering of Porto University, Porto, 458p
19. Veiga MR (2004) Wall coatings: functions and requirements (in Portuguese). LNEC/FUNDEC Course on Wall coatings pathology—ways to avoid it, Lisbon

20. LNEC (1996) Specialization course on wall coatings (in Portuguese). Veiga MR (coordination). National Laboratory of Civil Engineering, Lisbon
21. Flores-Colen I (2009) In-service performance evaluation methodology of rendered façades from the predictive maintenance viewpoint (in Portuguese). PhD Thesis in Civil Engineering, Instituto Superior Técnico, Lisbon, 486p
22. CSOPT (2004) RGE: general code of urban buildings (in Portuguese). Sub-commission for the revision of RGEU, Ordinance No. 62/2003 of January, Dispatch No. 5493/2003 of February the 27th 2004. Work document
23. Veiga R (2005) Performance of mineral binder façade coatings. Functional requirements and performance evaluation (in Portuguese). In: First national congress on construction mortars, Lisbon, CD
24. LNEC (1968) Recommendations for the execution of exterior mortar coatings (in Portuguese). Study integrated in the collaboration plan LNEC/HE-FCP, LNEC/MOP, Lisbon, 50p
25. Alves S, Sousa H (2003) Single-leaf exterior masonry walls (in Portuguese), 1st edn. LIDEL, Lisbon, 196p
26. Gaspar PL (2003) Methodology to determine the durability of current exterior renders (in Portuguese). MSc Dissertation in Construction, Instituto Superior Técnico, Lisbon, 209p
27. Kus H (2003) Service life of external renders. In: XXX IAHS—world congress on housing, Coimbra, vol III, pp 1875–1882
28. Vallée F, Blanchard N, Rubaud M, Gandini A (1999) Investigation on the behaviour of polymer-cement composites in ETICS renderings. In: Eighth international conference on durability of building materials & components, Vancouver, pp 1071–1080
29. Coelho AZ, Torgal FP, Jalali S (2009) Lime in construction (in Portuguese). TecMinho, Guimarães, 130p
30. Fontes A (2011) Influence of curing conditions in carbonation of traditional lime-based mortars—method of analysis (in Portuguese). MSc Dissertation in Civil Engineering, Instituto Superior Técnico, Lisbon, 165p
31. Green KM, Carter M, Hoff W, Wilson M (1999) The effects of lime and admixtures on the water-retaining properties of cement mortars. Cement Concrete Res 29:1743–1747
32. Veiga MR, Souza RH (2004) Evaluation methodology of free shrinkage of mortars since their casting (in Portuguese). Engenharia Civil 20:45–56
33. Baron J (1971) Fissuration du béton par hydratation localement différée du ciment. Laboratoire des Ponts et Chaussées, Paris
34. Sousa Coutinho AS, Gonçalves A (1994) Manufacturing and properties of concrete (in Portuguese), vol III. National Laboratory of Civil Engineering, Lisbon
35. Nsambu R (2007) Performance evaluation or repair mortars for reinforced concrete (in Portuguese). PhD Thesis in Civil Engineering, Instituto Superior Técnico, Lisbon, 503p
36. Gaspar P, Flores-Colen I, de Brito J (2007) Diagnosis techniques and loss of adherence anomalies classification in renders (in Portuguese). In: Second national congress on construction mortars, Lisbon, CD
37. Gomes AM (1995) Characterization of traditional mortars used in building exterior coatings (in Portuguese). PhD Thesis in Civil Engineering, Instituto Superior Técnico, Lisbon, 269p
38. Carasek H (1997) Factors that have influence on the adherence strength of mortars (in Portuguese). In: II STBA—Brazilian symposium of mortars technology, Salvador, pp 133–146
39. Miranda V (2004) Analysis of the adherence of solutions of traditional renders on concrete substrates (in Portuguese). MSc Dissertation in Construction, Instituto Superior Técnico, Lisbon, 147p
40. Scartezini L, Carasek H (2003) Factors that have influence on the tensile adherence strength of rendering mortars (in Portuguese). In: V STBA—Brazilian symposium of mortars technology, São Paulo, pp 133–146
41. Flores-Colen I, de Brito J, Branco FA (2009) In situ adherence evaluation of coating materials. Exp Tech 33(3):51–60

42. Galvão J (2009) In-situ test technique for the evaluation of the mechanical performance of façade renders. Sclerometer and ultra-sounds (in Portuguese). MSc Dissertation in Civil Engineering, Instituto Superior Técnico, Lisbon, 136p
43. Carneiro A, Cincotto M (1995) Requirements and performance criteria for a one-coat cement and lime coating mortar (in Portuguese). In: I STBA—Brazilian symposium of mortars technology, Goiânia, pp 326–337
44. Sá AFG (2005) Stone and lime wall renders (in Portuguese). MSc Dissertation in Construction, Instituto Superior Técnico, Lisbon, 186p
45. LNEC (2005) Rules to grant application documents to premixed mineral binder cement-based wall coatings (in Portuguese). Report 427/05. National Laboratory of Civil Engineering, Lisbon
46. Bastos P (2003) Deformation modulus of mortars—concepts and determination methods (in Portuguese). In: V STBA—Brazilian symposium of mortars technology, São Paulo, pp 27–40
47. Rodrigues PF, Henriques F (2003) Comparative analysis of current air limes (in Portuguese). In: Third ENCORE—third meeting on conservation and rehabilitation of buildings: materials and conservation and rehabilitation techniques, Lisbon, pp 503–510
48. Guerreiro C, Henriques F, Pinto AP (2007) Comparative analysis of moderately hydraulic air lime mortars and mixed binder mortars for renders of ancient buildings (in Portuguese). In: Second national congress on construction mortars, Lisbon, CD
49. Flores-Colen I, de Brito J, de Freitas V (2009) Expected render performance assessment based on impact resistance in situ determination. Constr Build Mater 23(9):2997–3004
50. Freitas VP, Torres MI, Guimarães AS (2008) Rising damp (in Portuguese). Collection Technical Documents, Faculty of Engineering of Porto University, Porto, 106p
51. Rato V (2006) Influence of the morphologic micro-structure on mortars performance (in Portuguese). PhD Thesis in Civil Engineering, Faculty of Science and Technology of New University of Lisbon, Lisbon, 294p
52. Schmid EV (1988) Exterior durability of organic coatings. FMJ International Publications Limited, Surrey, 334p
53. Quintela MA (2006) Durability of exterior one-coat wall renders (in Portuguese). MSc Dissertation in Buildings Construction, Faculty of Engineering of Porto University, Porto, 197p
54. Pena F (2008) Hydraulic lime mortars for wall coatings (in Portuguese). MSc Dissertation in Civil Engineering, Instituto Superior Técnico, Lisbon, 90p
55. Veiga MR, Aguiar J, Silva AS, Carvalho F (2004) Conservation and renovation of wall coatings in ancient buildings (in Portuguese). Collection buildings—conservation and rehabilitation. National Laboratory of Civil Engineering, Lisbon, 126p
56. Freitas VP, Pinto P (1999) Vapour permeability of construction materials—internal condensations (in Portuguese). Technical Information NIT 002—LFC, Faculty of Engineering of Porto University, Porto, 56p
57. Uemoto KL (1988) Pathology: damage caused by efflorescence (in Portuguese). Buildings Technology, Technologic Research Institute, Editor Pini, São Paulo, pp 561–564
58. Henriques FA (1992) Damp action in walls. Forms of manifestation, quantification criteria and analysis of repair solutions (in Portuguese). PhD Thesis in Civil Engineering, Instituto Superior Técnico, Lisbon, 378p
59. Neves C, Almeida AH, Lima J, Almeida T (1997) Influence of soluble chlorides and sulphates on mortars' properties (in Portuguese). In: II SBTA—Brazilian symposium of mortars technology, Salvador, CD
60. Lucas J (1990) Functional requirements of wall coatings (in Portuguese). ITE 25, National Laboratory of Civil Engineering, Lisbon, 116p
61. APICER, CTCV, DEC-FEUP, DEC-FCTUC (2003) Application manual for ceramic claddings (in Portuguese). Portuguese Association of the Ceramics Industry, Coimbra, 248p
62. Nero JG (2001) Renders—part I (in Portuguese). Arquitectura e Vida 20:112–117

63. Nero JG (2001) Renders—part II (in Portuguese). Arquitectura e Vida 21:90–95
64. Garcia J (2005) One-coat renders (in Portuguese). Technical application guide. Maxit, 38p
65. Rocha J, Gomes P, Lourenço J, Santos J (2009/2010) Working site report (in Portuguese). Buildings Construction Technology Course, IST, 60p
66. Marques MI, Rodrigues MP (1998) Paints, varnishes and paint coatings for construction (in Portuguese). National Laboratory of Civil Engineering, Lisbon, 111p
67. Louret M, Garcia P, Marques D, Aldeias J (2009/2010) Working site report (in Portuguese). Buildings Construction Technology Course, IST, 60p
68. Rodrigues P, Bezelga A (1996) One-coat coatings. Chapter 11—Wall coatings (in Portuguese). Construction general processes course. AEIST, IST, Lisbon
69. Rodrigues M, Eusébio MI, Ribeiro A (2005) Paint coatings. Defects, causes and repair (in Portuguese). National Laboratory of Civil Engineering, Lisbon, 43p
70. Magalhães AC (2002) Pathology of ancient renders (in Portuguese). Cadernos de Edifícios 2:69–85
71. Gaspar PL, Flores-Colen I, de Brito J (2006) Diagnosis techniques and classification of cracking in rendered façades (in Portuguese). In: PATORREB 2006—second meeting on buildings pathology and rehabilitation, Porto, vol II, pp 541–550
72. Sousa V, Pereira F, de Brito J (2005) Traditional renders: main degradation causes (in Portuguese). Engenharia Civil 23:5–18
73. Flores-Colen I, de Brito J, Freitas VP (2006) Expedient in situ test techniques for predictive maintenance of rendered façades. J Build Appraisal 2(2):142–156
74. Moropoulou A (2005) Integrated diagnosis using advanced in situ measuring technology. In: 10DBMC—international conference on durability on building materials and components, Lyon, CD
75. Veiga MR (2009) Compatible mortars. Characteristics to be reproduced and test methods (in Portuguese). In: Seminar on coating mortars in ancient buildings: contribution to their rehabilitation. ITECons, Coimbra

Gypsum Plasters

3

Jorge de Brito and Inês Flores-Colen

Abstract

This chapter includes a brief history of gypsum plasters. Then, several types of gypsum-based coatings are presented. Gypsum plasters' performance characteristics, in fresh and hardened state, are described, focusing on requirements, testing methods and standards. Design and construction recommendations are synthetized in terms of materials (binders, aggregates, admixtures and additions/fillers), design details/technical specifications for construction, and also characteristics of each coat in the plaster systems for traditional and industrial plasters. The pathology and diagnosis of these coating systems are characterised in terms of the common anomalies and probable causes. A classification of the diagnostic methods is presented. Maintenance and rehabilitation classification and strategies are discussed for plasters. Finally, American and European standards related with internal plasters and gypsum-based products are synthetized.

Keywords

Plasters • Gypsum • Performance • Design • Construction • Pathology • Diagnosis: maintenance • Rehabilitation • Standards • Gypsum-based products • Testing • Industrial plasters • Traditional plasters • Internal application

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M.C. Gonçalves, F. Margarido (eds.), *Materials for Construction and Civil Engineering*, DOI 10.1007/978-3-319-08236-3_3

3.1 Historic Introduction

The first applications of gypsum in construction date from the Neolithic period, e.g. in Çatal Huyuk, Turkey, circa 6000 AC [1]. The oldest remaining testimony from the use of gypsum by the Egyptians is the plaster of the pyramids (4000 to 2000 AC), even though in those times constructions were made of stone laid over stone without any kind of mortar [2]. Torraca [3] refers that hydraulic binders, as well as binders with some hydraulicity, can sometimes be found in large-volume ancient gypsum plasters. The Greeks might have been the first ones to use lime as coating mortar, essentially in painted gypsum plasters and wells' coatings [4].

It is mostly in Rome that gypsum plaster gains great expression and meaning. The Romans used the gypsum plaster's qualities (extreme plasticity, fast execution and reduced cost), imitating shapes and colours typical of other materials incomparably more expensive and harder and slower to work. Almost gone during the Middle Ages (with the exception of applications by the Arabs), gypsum plaster recovered its application as European architectonic decoration only in the Renaissance, starting in Italy, where the first big archaeological discoveries of the sixteenth century encouraged its rebirth [5].

The discovery of the history of gypsum plaster in Portugal is greatly hindered by the lack of documentation before the eighteenth century. The most ancient known Portuguese gypsum plaster work is from the sixteenth century (Manuel I period) and was made in a medieval twelfth-century construction, as decoration of the windows from the upper floor of the *Charola* of the Christ Convent Church in Tomar. Nevertheless, the most ancient vestiges of gypsum plaster in Portuguese territory are from the Roman times and were found, as fragments, in archaeological stations such as Conímbriga, Tróia or Freixo, near Marco de Canaveses [6].

However, gypsum plaster only started to be effectively divulged in Portugal in 1764, when the Marquis of Pombal created the Class of Plaster and Design, an activity that got together a group of Italian artists, where the Milanese João Grossi stood up as the director in charge. Many gypsum plaster works made in Portugal, such as the Palace of the Marquis of Pombal, in Oeiras, are attributed to this great master. The propagation of gypsum plaster gained such proportions that it started being currently used to imitate materials that are considered noble, such as marble or gilded wooden carvings [6, 7].

At the end of the eighteenth century, a new technique of making ceilings emerged, using nailed lathing, where the covings made with slender profiles were seen as a downsize of the classic Antiquity cornices. In Alentejo and Algarve, due to the dry and scarcely rainy climate, a type of external decoration emerged, referred to as mass ornaments, external gypsum plaster or *sgraffito*, whose execution technique bore some similarities to that of gypsum plaster but whose composition was completely different, since it did not include gypsum [6].

Influenced by the Romantic Movement, in the middle of the nineteenth century, a type of gypsum plaster decoration inspired in the literature and national exaltation emerged. Simultaneously, trying to mimic the aspect of the medieval and discoveries architecture, another type of gypsum plaster decorations arises in

Fig. 3.1 Pena palace [6]

Fig. 3.2 Montserrat villa [8]

Portugal linked with the Muslim and Manuel I art, exemplified by the Moorish plaster of the Pena Palace, in Sintra (Fig. 3.1), or the Montserrat Villa, also in Sintra (Fig. 3.2) [6].

Gypsum plaster decorations and ornaments assume great importance in the last decades of the nineteenth century and beginning of the twentieth century due to the Art Nouveau's influence, whose style features rely on asymmetry and fluid and artisanal shapes, making current ornaments be seen as exaggerated and very heavy. From then on, there was a fall of the decorative gypsum plaster [6].

In fact, the methods of design and application were changed in order to optimize the cost/quality ratio, ease and rate of execution, leading to sprayed plaster, based on factory premixed compositions. This was one of the factors that contributed to the present loss of the artistic character that gypsum plaster once won, even though its application scope increased, since it is used in every type of construction from controlled cost housing to office buildings of big commercial and services firms.

Recently, coatings based on synthetic binders that can be applied on interior wall and ceiling surfaces, known as synthetic plasters, emerged. They widely differ from "traditional" gypsum plasters in terms of composition, since they are made of synthetic resins dispersed in water (binder), even though their application presents several similarities.

3.2 Gypsum Plaster Classification

In order to put the current coatings object of this chapter into perspective, Table 3.1 presents the classification proposed by LNEC—Laboratório Nacional de Engenharia Civil (National Laboratory for Civil Engineering) [9, 10]—for coatings for interior wall surfaces, where the ones dealt within this chapter are shaded.

Table 3.1 Classification of the coatings for interior wall surfaces [9]

Functional classification	Main types of walls interior coatings
Smoothing coatings	Traditional renders
	Premixed renders
	Mixed binders renders
	Traditional gypsum and lime plasters
	Premixed gypsum plasters
	Synthetic premixed plasters
Finishing coatings	Traditional gypsum and lime plasters
	Premixed gypsum plasters
	Synthetic premixed plasters
Water-resistant coatings	Glued ceramic claddings
	Glued natural stone claddings
	Glued artificial stone claddings
	Epoxy coatings
	Synthetic binder coatings (enamels and varnishes)
Decorative coatings	Coatings in roll (paper, plastics, textiles and cork)
	Expanded cork agglomerate plates claddings
	Paint coatings

Table 3.2 Types of current gypsum-based coatings (EN 13279-1: 2005)

Designation	Code
Gypsum binder	A
Gypsum plaster	B
Gypsum building plaster	B1
Gypsum-based building plaster	B2
Gypsum-lime building plaster	B3
Lightweight gypsum building plaster	B4
Lightweight gypsum-based building plaster	B5
Lightweight gypsum-lime building plaster	B6
Gypsum plaster for plasterwork with enhanced surfaced hardness	B7
Gypsum plaster for special purposes	C
Gypsum plaster for fibrous plasterwork	C1
Gypsum plaster for bricklaying	C2
Acoustic plaster	C3
Thermal insulation plaster	C4
Fire protection plaster	C5
Thin coat plaster	C6

According to this classification, interior coatings fall within the following four categories:

- Smoothing coatings—to give the wall planeness, verticality and surface regularity
- Finishing coatings—to give the wall a smoothing complement, thus guaranteeing in most cases a pleasant visual look
- Water-resistant coatings—to provide the finishing coat in walls in locations where water is frequently present or cleaning is made by wet means
- Decorative coatings—to provide the aspect intended by the users in terms of visual comfort, when the underlying coats do not do it by themselves

In order to present a more specific classification of current gypsum-based coatings, Table 3.2 shows the classification proposed in standard EN 13279-1: 2005.

Similarly, for synthetic coatings, Table 3.3 presents the classification included in Veiga et al. [11] for walls and ceilings' interior surfaces.

The historic introduction leads to the following global classification that will be used in the next sections:

(a) Traditional gypsum plasters made according to ancestral proceedings
(b) Premixed gypsum plasters, whose constituents are all preselected and mixed in the factory and are applied on-site by spraying
(c) Premixed synthetic plasters, whose composition includes synthetic resins

Table 3.3 Classes of synthetic binder coatings for interior wall surfaces [11]

Classification criterion	Coating classes	Characteristics	
		Filler size (μm)	Coat thickness (mm)
Size grading	Current size grading	>250	–
	Fine size grading	<250	
	Very fine size grading	<100	
Current application thickness	Sealing	–	>5
	Liners		5-2
	Skins		2–0.5
	Films		≤0.5

3.3 Functional Requirements and Performance Parameters

The Community Directive relative to construction products (CPD), 89/106/EEC of December 21 and 93/68/EEC of July 22, transposed to the Portuguese context by Decree-Law 113/93 of April 10, changed by Decree-Law 4/2007 of January 8, establishes the following six essential requirements for building construction works (that include various products, materials and systems): stability (EE1); safety against fire risks (EE2); hygiene, safety and environment (EE3); safety in use (EE4); protection against noise (EE5); and energy savings (EE6), taking into account an economically viable period and current maintenance. This Directive (CPD) is repealed by the Construction Products Regulation (CPR) No. 305/2011 of the European Parliament and of the Council of March 9, 2011 laying down harmonized conditions for the marketing of CPD and that includes another essential requirement-related conditions with sustainable use of natural resources.

Next, the specific performance requirements in the hardened state that each of the coatings dealt with in this chapter (current interior gypsum plasters, from now on called CIGP) must comply with, when applied in walls and ceilings of interior surfaces, are presented. The sections are divided into gypsum-based coatings (traditional and premixed plasters) and synthetic binder-based coatings.

3.3.1 Gypsum-Based Coatings

Based on the literature analysed, a set of performance parameters was defined, referring to the coating system as a whole (smoothing coat, finishing coat and paint finish, considering that gypsum coatings may be exposed or be painted with a non-textured paint).

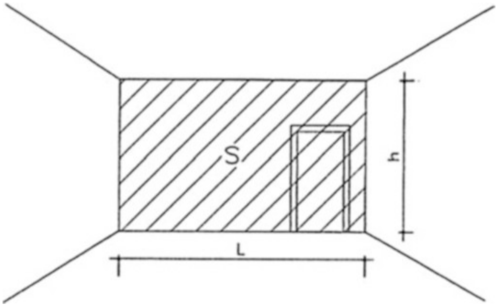


Fig. 3.3 Wall panel [12]

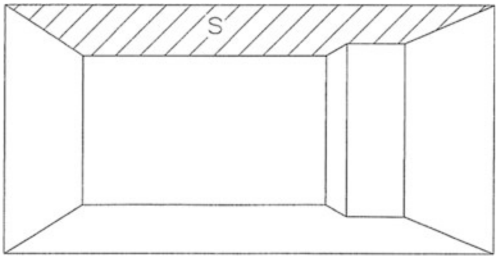


Fig. 3.4 Ceiling panel [12]

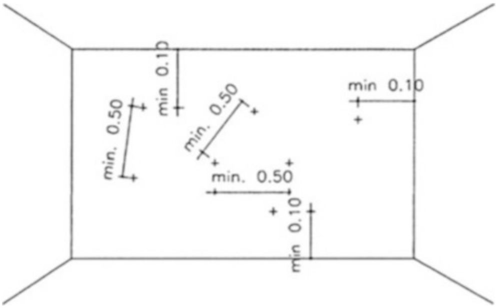


Fig. 3.5 Samples' location [12]

3.3.1.1 Thickness and Hardness

The thickness of the coating influences its smoothing capacity and mechanical strength. According to DTU No. 25.1, the thickness of a coating must be determined based on samples in panels (wall or ceiling). In the case of walls, a panel must have an area with a height (*h*) equal to the distance from the ceiling to the pavement and a width (*l*) equal to the distance between two adjoining edges or angles (Fig. 3.3). As for ceilings, the panel's area (*S*) is defined by the walls and the angles (Fig. 3.4). In either case, the openings in the surfaces are not deducted.

The number of samples to be made is $S/1.5\ \mathrm{m}^2$, with a minimum of 5, and there is no need for them in panels with $S < 1.5\ \mathrm{m}^2$ or $l < 1.5$ m. The samples' location must be at least 0.50 m apart and 0.10 m from the borders of the panels or intermediate edges (Fig. 3.5).

Each sample is made by lightly puncturing the coating until reaching the substrate or, in softer substrates (e.g. autoclaved aerated concrete or expanded polystyrene), from cores extracted from the wall.

The average coating thickness is obtained by the arithmetic average of the samples made, after eliminating the extreme values when the number of samples exceeds 6. The minimum thickness value should not be lower than 8 mm, in current coating execution, or 12 mm if the points and lines technique is used.

To determine the hardness according to DTU No. 25.1, the panels made to assess the thickness are used. This operation only starts after the coating is well dried (water content below 1 %, corresponding to around 3 weeks to 1 month after execution), and a Shore C hardness measuring device must be used. To make the tests, 0.2-m circles are defined centred with the thickness samples' location, and six measurements are taken in each circle. The two extreme values are eliminated, and the hardness value of each area is obtained by the arithmetic average of the remaining four values determined. The hardness of the panel's coating is obtained by the arithmetic average of the hardness in various areas. For sprayed gypsum plasters, the hardness of each area must be higher than 60 Shore and the average hardness in the panel should not be less than 65 Shore.

According to standard EN 13279-1: 2008, only in gypsum-based coatings with improved surface hardness is a minimum hardness value (surface resistance) of 2.5 MPa required, determined according to the test procedures proposed by EN 13279-2: 2004.

3.3.1.2 Planeness, Verticality and Surface Regularity

These three performance parameters strongly depend on the performance of the gypsum plaster applier. In the case of surface regularity, the final result is also related to the size distribution of the product (in powder), i.e. the greater its fineness, the easier it will be to get a regular surface (less rough). The assessment criteria and tolerances for these parameters are those specified in DTU No. 25.1.

The planeness and verticality characteristics of the surfaces must be specified in the tender of each work. Planeness can be split into global and local. In the first case, applying a ruler 2 m long over the surface should not lead to a planeness deviation higher than 10 mm between the most salient point and the most re-entrant point. This limit is reduced to 5 mm when the coating is executed using the points and lines technique. To evaluate local planeness, the procedure is similar, with the exception of the ruler's length, which is 0.20 m, and the maximum deviation, which is 1 mm. The verticality deviation measured over a vertical length of 2.50 m should not exceed 5 mm (Fig. 3.6). Furthermore, the requirements of planeness and verticality are only applied when the substrate has no deviations greater than twice the equivalent values of the coated surface.

The surface regularity generally defines whether the surface is smooth or rough. From a functional viewpoint, preference is given to smooth surfaces, exempt of visible cracks and grooves or recesses deeper than 1 mm, because they accumulate less dirt, have lower retention of surface damp and are less prone to the attachment and development of moulds.

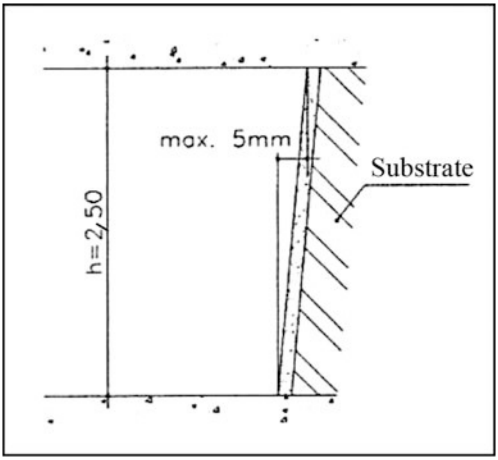


Fig. 3.6 Verticality tolerances [12]

Fig. 3.7 Pull-out test and adhesive failure in the interface between the ceiling's gypsum coating and the concrete substrate

3.3.1.3 Adherence to the Substrate

The evaluation of the adherence of the coating to the substrate may be done according to the method in specification form Fe Pa 36 from LNEC ("adherence to the substrate under dry conditions", based on Cahier No. 1779 from CSTB), i.e. through a pull-out test with a dynamometer (Fig. 3.7), when the coating is new or after it has been dampened with water and then dried. In the first case, the pull-out stress of the new coating must be higher than 0.5 MPa and in the second case higher than 0.35 MPa [12, 13].

The standard EN 13279-1:2008 refers that the pull-out stress (related to adhesive failure) must be higher or equal to 0.1 MPa, determined according to the test method proposed in EN 13279-2: 2004.

3.3.1.4 Flexural and Compressive Strength

Based on the values and tests from standard EN 13279-1:2008 (test methods in EN 13279-2), the flexural strength must be higher than 1.0 MPa, unless it is a gypsum-based coating with improved surface hardness, for which the limit is raised to 2.0 MPa. The compressive strength must be higher than 2.0 MPa, except for gypsum-based coatings with improved surface hardness, for which the limit is raised to 6.0 MPa.

3.3.1.5 Resistance to the Attachment and Development of Moulds

CIGP located in damp and badly ventilated rooms or over thermal bridges of any surface in contact with cold spaces are prone to the attachment and development of moulds. As a matter of fact, in these locations, the coating must be protected by a fungicide, which must be incorporated in the finishing coat of exposed coatings through a fungicide admixture, or in the most current case when there is paint finish, the latter must have fungicide properties. However, these preventive solutions have the disadvantage of being temporary, according to the product and content used [10, 13].

A very efficient solution is to guarantee proper ventilation and strengthen the thermal insulation of the thermal bridges, in order to prevent, respectively, prolonged dampening and condensations in those areas. The high water permeability of the whole coating system is equally very important in the prevention of the attachment and development of the referred microorganisms and can be evaluated using the test form Fe Pa 17 from LNEC ("water vapour permeability test") [10, 12, 13].

Another aspect to be remembered is that smooth surfaces make it difficult for moulds and various types of dirt to attach themselves, and therefore they must have precedence over rough surfaces, especially in the environments described above [10, 13].

3.3.1.6 Other Performance Parameters

These coatings must be resistant to alkali attack and degradation actions due to use, namely, shock, friction, water and dirt. These performance parameters are developed in the section dedicated to synthetic plasters. On the other hand, these coatings are classified, without testing, in fire reaction class A1 (i.e. there is no contribution to the development of fire), when they have less than 1 % of organic matter relative to their weight or volume (EN 13279-1: 2008); when required, the thermal resistance of a gypsum-based coating system must be determined according to EN ISO 6946:2007.

3.3.1.7 Durability

The expected service life of a coating of this type is around 30 years, as long as during this period, it is subjected to periodic maintenance operations. Nonetheless, durability is very dependent on the exposure/protection degree from biologic agents and from shock, friction, water and dirt actions [10].

3.3.2 Synthetic Binder-Based Coatings

As referred for gypsum coatings, the quality demands from synthetic plasters refer to the set made of the smoothing coat, finishing coat and eventually varnish paint or non-textured paint.

3.3.2.1 Resistance to Saponification

Strictly speaking, saponification is the designation adopted for the degradation process of an oil paint that consists of the formation of a soap and an alcohol as a consequence of the reaction between the oil and the bases. However, in synthetic plasters, products based on a dispersion of synthetic polymers, if degradation by alkaline attack of this type were to occur, the result would not be a soap but rather an alcohol; thus, the correct designation of the phenomenon would be hydrolysis [13].

Synthetic CIGP should not be affected by the substrates' alkalinity. Therefore, these coatings should be tested in a substrate dampened by an alkaline solution, from which no detachment or any other type of degradation should result [13].

3.3.2.2 Planeness, Verticality and Surface Regularity

Concerning these parameters, synthetic CIGP should comply with the requirements defined in Sect. 3.3.1.2.

3.3.2.3 Adherence to the Substrate

The evaluation of the adherence of these coatings to the substrate may be made through the tests described in Sect. 3.3.1.3 and on a peeling test under dry conditions. In the latter, the synthetic coating is applied over strips of net previously fastened to the substrate. After enough time for the synthetic products to harden has gone by, the net strips are peeled off, and the resistance of the coating to this pulling-out action is registered. It should be greater than 0.5 N/mm of the width of the net strip [13].

3.3.2.4 Resistance to Degradation Actions Due to Normal Use of the Spaces (Shocks, Friction, Water and Dirt)

The performance parameters relative to actions of shock (of a hard object, cutting and non-cutting), friction, water and dirt (of domestic chemical products) depend on the type of building, spaces, use and users' access level [13].

To evaluate the resistance to shock actions, the sphere shock test (Fig. 3.8) and the grid cutting test (Fig. 3.9) are used. The former corresponds to the action of a 250 g sphere, with a pendulum movement of 0.80 m span. The latter consists of the shock action of an indented steel block ignited by additional progressively heavier masses, 250, 500 and 1,000 g, with a pendulum movement of 0.80 m span, indenting a grid on the coating's surface. In the sphere shock test, the diameter of the dent made must be lower than a given limit, and in the grid cutting test, none of the small squares defined by the indented grid should detach itself for a minimum value of the additional mass. In the grid cutting test, if the coating does not

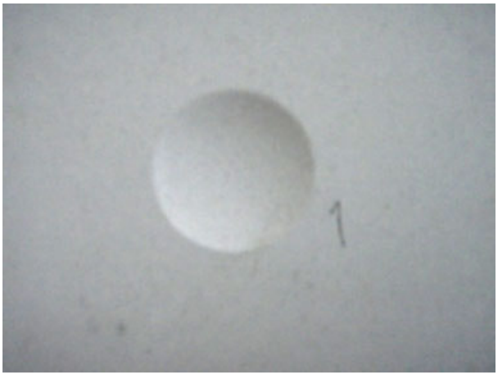


Fig. 3.8 Sphere shock test [13]

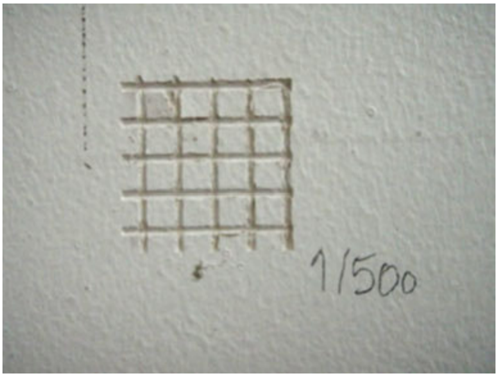


Fig. 3.9 Grid cutting test [13]

withstand the action of the steel block for a 250 g mass, it will be classed with a resistance index of 0 (zero) [13].

To determine the friction resistance, the edge of a disc moving in a straight line and loaded with additional progressively heavier masses, 250, 500 and 1,000 g, is pressed against the coating. The appraisal of these effects defines the degree of satisfaction of scratching, abrasion and polishing (if the surface is painted). The two first tests correspond, respectively, to the numerical values of the heavier additional mass for which the disc does not scratch the coating (or, if it does, it does not detach it) and does not make a significant groove on its surface. In both tests, if the coating does not withstand the least severe action (no additional mass), the index assigned will be "zero". The polishing test determines whether the paint becomes shinier in the area under friction. If it does, it will be assigned the designation of "unsatisfactory" and in the opposite case it will be "satisfactory" [13].

To evaluate resistance to water, the procedure is the same as for the friction resistance but without the additional mass over the coating. Its surface must be previously dampened by a kaolin paste that remains in contact with the coating for progressively longer periods—5, 15, 30, 45 or 60 min. The performance after dampening is measured by the numerical value of the longest period of contact

Fig. 3.10 Dirt resistance tests using staining products [13]

between the paste and the coating for which the coating shows no traces of detachment. It will be classified as “unsatisfactory” if it does not withstand the least severe action (5 min) [13].

Dirt resistance is evaluated through the action of conventional staining products or others whose action on the coating is predictable and subsequent cleaning action to remove the stains (Fig. 3.10). To perform the test of resistance to stain formation, some conventional typical products are necessarily used (the letter that precedes the designation of the product corresponds to its code in Table 3.4) [13].

The removal of staining products can be made using the instructions given by the coating manufacturers or the following procedures: (1) apply a dry sponge; (2) apply a sponge dampened with water; (3) apply a sponge dampened with water with neutral liquid detergent; (4) light sanding of the surface; or (5) use a school eraser. In the strictest sense, the test result consists of the characterization of the remaining degradations attributed to each of the staining products after trying to remove the stains (e.g. light stain, pronounced stain and surface corrosion). However, out of the results presented in Table 3.4, only the code of the current products that do not stain the coating is referred to [13].

Table 3.4 shows the limits accepted in the tests described for interior walls in the various spaces of a housing building. If any given cell has a dash (–), the coating must have the capacity to withstand the most severe action of the corresponding test. The requirements of resistance to grid, scratching and abrasion depend on the intensity of users’ circulation, the number of users per house, the existence of children and the size of the space. If the kitchens and bathrooms’ ventilation is efficient, the requirements of resistance to water and dirt can be reduced if the surfaces are located more than 2 m from the ground level. Even though Table 3.4 applies to interior wall surfaces, it is reasonable to extend its application to ceilings. These must be looked upon as surfaces more than 2 m above the ground level slab in terms of resistance to shock, friction and dirt actions and as surfaces less than 2 m above that level for evaluation of water resistance purposes.

3.3.2.5 Resistance to the Attachment and Development of Moulds

The requirements concerning resistance to the attachment and development of moulds are identical to the ones referred in Sect. 3.3.1.5 for current gypsum-based coatings.

3.3.2.6 Durability

The service life demanded from a synthetic binder coating in interior surfaces is at least 10–12 years, as long as during that period, the necessary periodic maintenance operations adequate to this type of coating are guaranteed [13, 14].

Table 3.4 Resistance requirements to shock, friction, water and dirt actions applied to interior surfaces of housing walls, using the *Martinet Baronnie* technique [13]

	Test action						
	Shocks		Friction				
Type of space	Sphere shock Φ (mm)	Grid cutting index (g)	Scratching index (g)	Abrasion index (g)	Polishing wall	Water index (min)	Dirt index
Sleeping room	20	–	–	–	–	–	a
Living room	20	–	–	–	–	–	a
Circulation spaces inside a house (corridors, halls)							
(1) Surfaces more than 2 m high	20	–	–	–	–	–	a
(2) Surfaces below 2 m high	20	250 or 500	250 or 500	250 or 500	Satisfactory	5 min	a, b, c, d, e
Kitchen	20	–	250	250	–	60 min	a, b, c, d
Bathroom	20	–	250	250	–	60 min	a, b
Spaces to wash clothes	20	–	250	250	–	60 min	a, b
Surfaces in frequent contact with hands (surfaces contiguous to switches, hand railings, among others)	20	250	250	250	Satisfactory	5 min	a, b, c, d, e
Collective circulation spaces (corridors, halls of common areas, staircases, among others)							
(1) Surfaces more than 2 m high	20	250	250	250	–	–	a
(2) Surfaces below 2 m high	15	500	500	500	–	60 min	a, b, c, d, e
Collective spaces of garbage collection or disposal	20	250	250	250	–	5 min	a, b, c, d

3.4 Design and Execution

In this section, the design and execution procedures are described separately for traditional and nontraditional gypsum plasters (the latter including gypsum and synthetic binder plasters).

3.4.1 Constituent Materials

Traditional gypsum plasters are made of binders (dark or white gypsum and slaked air lime in powder or paste), mineral fillers (clean and very fine sand, siliceous or limestone), admixtures (setting retarders, hardeners), water and eventually additions (pigments).

Premixed plasters are made of binders (dark or white gypsum and slaked air lime in powder and resins), mineral fillers (clean, dry and calibrated sand; limestone powder), admixtures (setting retarders, plasticizers and water retainers), water and other additions (e.g. pigments, mineral fibres).

3.4.1.1 Gypsum

Gypsum was the artificial binder used to make the most ancient mortars, applied in masonry by the Babylonians and Egyptians more than 4,000 years ago. It is essentially a binder of dry climate countries, since it has a poor performance in the face of environmental humidity, which leads to its deterioration.

Gypsum powder results from a sedimentary rock composed essentially by bi-hydrated calcium sulphate ($CaSO_4 \cdot 2H_2O$), of various colours, from pure white to yellow, grey or rose, according to the impurities within. Gypsum stone is sufficiently soft to be scratched by a nail and cannot be applied in stonework or masonry [6]. According to its greater or lesser purity, gypsum may have the following shapes [15]:

- Crystalline, in great translucent crystals (alabaster) or transparent and colourless (selenite), shaped as spears or as scales
- Fibrous, when almost pure, making parallel silken needles
- Earthen, with 10–12 % of clay impurities

To make powder gypsum, the purest rocks are used: selenite ($CaSO_4 \cdot 2H_2O$), anhydrite ($CaSO_4$) and alabaster. They are submitted to heat action, loose water and become a powder, light coloured and uniform, unctuous to the touch, which sets and hardens very fast when in contact with water [6]. In the past gypsum was made in artisanal kilns, whilst nowadays it is made in industrial cylindrical kilns by heating in water vapour after a milling process.

Gypsum used as binder in plasters and mortars is obtained by burning gypsum stone at temperatures from 130 to 170 °C, made fundamentally of hemi-hydrated calcium sulphate ($CaSO_4 \cdot 1/2H_2O$):

$$CaSO_4 \cdot 2H_2O + \text{heat} \rightarrow CaSO_4 \cdot 1/2H_2O + 3/2H_2O$$

3.4.1.2 Air Lime

Resulting from burning the purest limestone, air lime was until the beginning of the twentieth century the most used binder. Air lime results from the decomposition, at temperatures of 800–900 °C, of limestone with at least 95 % of calcium carbonate ($CaCO_3$) or calcium carbonate and magnesium ($xCaCO_3 + yMgCO_3$), with impurities below 5 % [16, 17].

Air limes are divided into calcic or magnesian (a 20 % content of magnesium oxide in the raw material is the lower limit for a lime to be classified as magnesian). Calcic limes are subdivided into [6]:

- Fat lime—when the limestone is made of at least 99 % of calcium carbonate
- Lean lime—when the limestone has a content of clay and other impurities of 1–5 %

The product obtained from burning is called quicklime (calcium oxide, CaO) and mixed with water provides slaked lime (calcium hydroxide, $Ca(OH)_2$):

$$CaO + H_2O \rightarrow Ca(OH)_2$$

The process of making lime went through an evolution similar to that of gypsum from artisanal kilns to industrial plants.

3.4.1.3 Synthetic Binders

In synthetic plasters, the binders are made of synthetic resins, of which the ones most used in current synthetic coatings are the thermoplastic, whose shape can be modified by heating without changing its constitution (they are soluble only in adequate solvents), namely, those in the family of acrylates and vinyl acetates plain or copolymerized, such as [18] polyvinyl acetate, polyvinyl acetate-*co*-vinyl, polyvinyl acetate-*co*-styrene, vinyl versatic *co*-acrylic polymer and copolymer styrene butadiene acrylic.

Products based on acrylic resins have some advantages relative to products based on vinyl resins, such as greater resistance to ageing due to atmospheric agents [18].

3.4.1.4 Mineral Fillers

Sand used in gypsum plasters must be very fine, siliceous or limestone, very light coloured and exempt of organic impurities and soluble salts. If its clay content is higher than 6 %, sand must be rejected [6].

Organic matter may retard or partially stop setting, and soluble salts may cause efflorescence. Clay is tolerated up to a given content, in order to confer workability; however, in excess it may cause an inconvenient drying shrinkage.

Sands used in traditional gypsum plasters are siliceous, harder, less porous and with great chemical inertia, and limestone is less resistant and more deformable.

Sedimentary sands, from the sea or river, are also used, but if they are imperfectly washed, they lead to subsequent problems [19].

Mineral fillers used in premixed plasters are natural, mostly from calcite (calcium carbonate) or quartz (silica), whilst fillers of dolomite, hydrated calcium sulphate, barite (barium sulphate), talcum, kaolin, among others, are used less frequently.

3.4.1.5 Water

The water used in gypsum mortars and pastes must be potable and be free of impurities or harmful salts. Water containing sodium chloride, magnesium or potassium in contents higher than 1 % or sulphates over 3 % [20] must not be used because they hinder the mortars' strength. The same happens with water containing organic substances, such as wells or swamp stagnated water.

3.4.1.6 Additions (Pigments)

In traditional gypsum plasters, natural pigments are used, made of mineral earths with oxides, sulphites and carbonate, metallic or coming from plants and animals [6].

Pigments used in premixed plasters are mineral or organic, generally white coloured, even though they can also be marketed in other light colours, such as cream, beige, green or rose, the latter always applied in the finishing coat. A pigment must have good characteristics of opacity (resulting from the difference between the refraction indexes of the pigment and the binder and increasing with that difference), dyeing capacity, fineness and light and heat stability [18, 21].

3.4.1.7 Admixtures

The admixtures used in traditional gypsum plasters were, among others, setting retarders (dextrin, glue, concentrated sodium silicate, hydraulic gypsum), hardeners (alum, zinc sulphate, potassium silicate) and traditional setting retarders and hardeners (strong glue, fish gum and gelatine) [6].

The admixtures used in premixed plasters can be classified as [18]:

- Dispersant (e.g. lecithin)—to facilitate the dispersion of products in the liquid phase
- Wetting (e.g. oleic acid)—to favour the enveloping of solid constituents by dispersion by decreasing the interfacial stress between the solid and the liquid phases
- Thickeners (e.g. colloidal silica)—to increase the consistency of the products in paste
- Fungicides and anti-moulds (e.g. copper acetoarsenic)—to stop the attack of the coating by fungi or moulds
- Anti-sedimentation (e.g. bentonite)—to prevent sedimentation of the solid constituents during stocking
- Antifoam (e.g. octyl alcohol)—to prevent the formation of foam during application

- Anti-skin (e.g. hydroquinone)—to prevent the formation of skins on the surface of the products during stocking
- Drying (e.g. lead naphthenates)—to shorten the time needed for the coatings to dry

3.4.2 Traditional Gypsum Plasters

Among the traditional gypsum plasters, there are several types of coatings [10]:

- Gypsum paste (pure gypsum paste)
- Gypsum mortar (gypsum and sand)
- Gypsum and slaked lime (with or without sand)

3.4.2.1 Constitution

Traditionally in Portugal, gypsum-based coatings are applied on a substrate after it has been coated with a render, whose function is to smooth and prepare the surface for the execution of the finish. However, if the substrate's surface is very irregular, such as rough stone masonry (a frequent situation only in ancient buildings), it is necessary to previously smooth the surface by applying filling mortar in the most depressed areas [10].

The characteristics of the substrate determine the number and constitution of the coats to be used. The quality of execution of the substrate determines the number of coats needed to obtain a plane surface, thus influencing the coating's thickness. The texture, porosity and suction of the substrate influence its adhesion capacity to the overlying layer, determining the content of the mix to use. However, if great water contents are used in the coating's execution to decrease suction propensity, efflorescence may occur later on the coating's surface. The strength of each coating layer must decrease from the substrate outwards, to prevent potential cracking and loss of adherence [10, 22].

Therefore, the layers to be used are (Fig. 3.11):

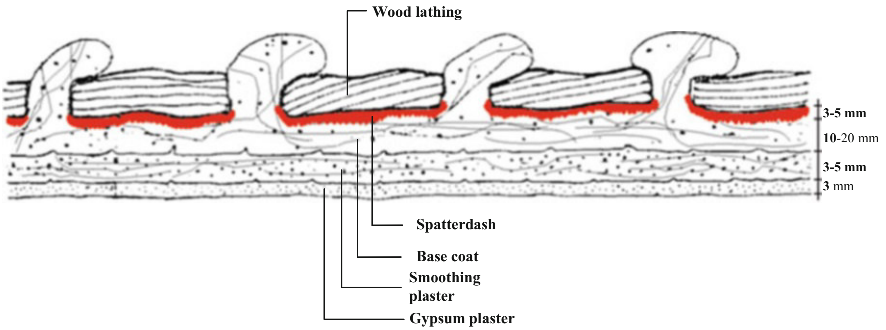


Fig. 3.11 Coats of a traditional gypsum plaster (adapted from [15])

- Spatterdash, 3–5 mm (cement and sand)
- Base coat or undercoat
  - Single layer, 10–15 mm
  - Double layer (filling mortar and “mortar”), 20 mm
- Finishing coat (6–8 mm)
  - Smoothing plaster, 3–5 mm (lime and sand paste + gypsum or simply gypsum and sand)
  - Gypsum plaster, 3 mm (gypsum and slaked air lime paste or simply gypsum with setting retarder)

The main function of the spatterdash is the preparation of the substrate for the application of the next coat, ensuring a good adherence thanks to its rough surface. Spatterdash is a discontinuous coat, with maximum thickness between 3 and 5 mm, and is made of a mortar with a high cement content (e.g. a volumetric proportion of 1:2 (cement-sand)) and with enough water to guarantee cement hydration and that the substrate’s absorption is even. The spatterdash can be applied by slapping it against the wall with a broom dipped in mortar or mechanically by spraying. When this coat is being applied, the substrate must be clean and dampened [10].

The base coat, also called undercoat, has its main function of smoothing the surface, ensuring verticality, planeness and unwarping of the walls and being the final barrier against humidity from the exterior or the substrate. Furthermore, it must confer a good adherence to the subsequent coats. The final thickness of the base coat must be within the 10–15 mm range, for single-layer applications, and may reach 20 mm if two layers are applied (filling mortar and “mortar”), which is necessary when the substrate is very irregular. The mortar to be applied must be mixed binder, with volumetric proportions between 1:0.5:4 to 4.5 and 1:1:5 to 6 (cement-lime-sand), always complying with the decreasing trend of binder content from the inside outwards [6, 10, 23].

The application must start after the spatterdash’s mortar has developed most of its initial drying shrinkage (a minimum of 3 days) and is made manually by slapping the mortar against the substrate and uniformly pressing it with a trowel. The roughness of the base coat’s surface must be compatible with the finishing coat to be applied. If the base coat is made with two layers, the latest remark applies only to the second layer, which is under normal circumstances applied after the first layer has developed most of its initial drying shrinkage and is then dampened [10, 23].

When a metal or fibre glass reinforcement is applied, the base coat must be made with two layers, where the first one is applied with pressure in order to penetrate through and involve the mesh and the second one is made after the first one completely dries and hardens [10].

The finishing coat is applied in two layers, the first one called smoothing plaster and the second one gypsum plaster, with a total thickness between 6 and 8 mm.

The composition and volumetric proportion of the mix is different: in the first one, it is 1:2:1 or 1:1:4 (gypsum-slaked lime paste-sand) and in the second one 1:0 to 0.25:0 to 1 (gypsum-slaked lime-sand) [10].

The smoothing plaster prepares the surface for the application of the final finishing coat (gypsum plaster). It must be applied with a trowel, starting from the border (lower in the case of walls), then spreading the mortar onto the wall's upper area with the trowel, until the opposite border is reached.

The plaster is obtained by mixing the lime paste with the sand, adding the gypsum only immediately before application, due to its short setting time. This mix allows a useful application period between 10 and 30 min [10].

In the case of walls, the points and lines technique can be used. To that purpose, gypsum points (markers) are made on the wall, starting from the upper level of the wall and coming down. Their horizontal spacing should be around 2 m and the vertical spacing between 1.5 m and 2.5 mm. Next, the points in the same vertical line are united by mortar strips, forming the lines, and then the area in between each two consecutive lines is filled with mortar, later smoothed with a ruler [6, 23].

The gypsum plaster's main purpose is to give the surface its target final aspect. To that purpose, this coat must generally have a smooth finish, even though it may incorporate frame and ornaments, in which case it is considered a decorative coating. Similarly to the previous coat, the gypsum plaster is applied with a trowel. However, being the final coating layer, its finish is more demanding, with a plasterer's spoon or a small trowel. When a plain gypsum paste is used, mixing is done in a large bowl where the amount of water necessary (50–70 % of the gypsum's volume, around 18 L per 25 kg of gypsum) is previously poured. Then the powder gypsum is sprayed on it in small layers until they become saturated, and that is when the paste is quickly mixed and application starts at once. Sometimes slaked lime is added to the gypsum or gypsum is mixed with lime water with the objective of decreasing its expansibility, increasing its hardness after drying and/or for economic reasons (lime is less expensive than gypsum) [6, 10, 24].

Traditional gypsum plasters can have several types of final finish (Figs. 3.12, 3.13, and 3.14): polishing; painting; colouring the plaster itself; decorative elements (frames, moulded ornaments, painted ornaments, fresh painting and faked painting); and stucco (imitation of marble or other natural stones) [6, 10].

Fig. 3.12 Frames around a moulded ornament in a plastered ceiling [25]

Fig. 3.13 Painted ornaments in plastered wall [25]

Fig. 3.14 Painting in plastered ceiling and plaster strip in wall, imitating a natural stone [25]

3.4.2.2 Application On-Site

Notwithstanding their vocation as substrates characteristic of ancient buildings (masonry walls, timber and masonry partition walls—Figs. 3.15 and 3.16), it can be said that traditional gypsum plasters have characteristics to be applied in any type of substrate, as long as adequate underlying coats are applied, in terms of the number and proportion of their constituents. In LNEC [10], three main types of substrate are identified:

- Continuous substrates—the application of gypsum plasters is made after that of a render. Within this type of substrate, there are concrete and brick masonry and expanded clay and concrete blocks; the former are strong, with small to medium porosity and small to medium suction, depending on the density; the adherence of the render to the concrete varies according to the latter's surface, which is very dependent on the type of formwork used; to improve the adherence in surfaces too smooth, the concrete's surface needs to be treated; masonries usually have some suction and mechanical adherence, with the exception of bricks or blocks of high density, which may need a surface treatment, or lightweight concrete masonries, where special care must be taken so that the render is not stronger than the substrate.

Fig. 3.15 Timber framing nogging masonry wall in pombaline building [25]

Fig. 3.16 Timber lathing over partition wall in pombaline building [25]

- Plate or panel substrates—there are panels or plates of gypsum (with sisal fibres) and plates of cork or glass wool; the former do without the application of render and gypsum plaster in this type of substrate which is made with gypsum paste, in both finishing coats; the joints between gypsum plates are covered with gypsum filling; however, the humidity level of the plates should not be too high since that causes cracking of the finish, neither too low because that would lead to visible joints; on the other hand, substrates of cork or glass wool plates have no risk of drying shrinkage, if dry; the cork plates have low suction and varying adherence, which can be improved by spraying a fluid paste of cement and sand or by using a galvanized steel mesh fastened to the surface; the glass wool plates have low suction and good adherence, but when they are fastened to concrete slabs and the goal is to coat them before they dry completely, it is necessary to reinforce the joints with a metal mesh or incorporate the mesh in the coating, in order to prevent cracking of the coating along the joints.
- Grid substrates—even though providing a good global adherence, they require the application of a smoothing coat with the purpose of making the substrate continuous; with metal grids, it is necessary to apply an anticorrosion treatment (paint with anticorrosion paint or adequate metal treatment such as galvanizing).

Traditional gypsum plasters are fit to coat the interior surfaces of the walls and ceilings in dry spaces for private or public use, as long as in the latter case, they are located at least 2 m above the floor level; otherwise, they should receive an adequate treatment. The use of this type of coating is discouraged in locations that may have been subjected to an intense and prolonged rain action [10].

It should be guaranteed that ambient temperature during application of the coating is at least 2 °C and that the temperature of the substrate is between 5 and 40 °C. The substrates should be dry and free of dust, efflorescence or oils that may hinder the adherence between coats. The irregularities of the substrate that are not overcome by the smoothing coats should be the object of the previous treatment, to curb the protrusion and fill the gaps. Discontinuity of the substrate equally deserves special attention, i.e. in the juxtaposed substrates of different nature, good practice implies the incorporation over the joint of a metal mesh protected against corrosion or a vegetable or glass fibre net at least 15 cm past each side of the joint, thus minimizing the risk of cracking [10].

At the stage of work planning, the time needed to apply all the coats must be taken into account, as well as the waiting times in between; in this case, the importance of the coats with cement being completely dry when the finish is applied, in order to eliminate the chance of gypsum reacting with cement, leading to expansive salts, is stressed. It is also necessary to allocate an adequate time interval for the masonries to settle (usually around 1 month). Furthermore, the works can be phased so that the plastered surfaces are not damaged by the nature of any subsequent works or due to weather exposure. Any changes on-site must be made before the surfaces have their final finish applied. All surfaces that are finished with traditional gypsum plaster should be identified in order to apply the adequate underlying coats. Even though it has some undesirable environmental impacts, a conservative stance of not reusing gypsum that has already set, even by adding fresh gypsum, should be adopted, to prevent cracking. The mixing water whenever possible must be tap water, and salty or stagnated water should never be used. Sand must not contain soluble salts or impurities in suspension. Every tool used in the application of the various coats should be clean, especially those used in the final gypsum coats. Every metal element that may be in contact with the coating must be protected by applying an anticorrosion paint or an adequate metal treatment, such as galvanizing. In convex angles, the use of corner protections is recommended: metal (in this case, protected against corrosion) or plastic brackets, fastened to the edges with gypsum [10, 12].

3.4.3 Nontraditional Plasters

Compared with equivalent traditional coatings, nontraditional plasters have several advantages presented next [11]:

- Faster application, especially due to doing without previous smoothing of the surfaces, namely, smoothing mortar, “mortar” and smoothing plaster in masonry walls; in mixes applied mechanically, the reduction of the number and qualification of the labour force allows greater yields at the working site, as long as planning ensures that works are continuous.

- Greater setting time (the beginning of setting time generally takes at least 45 min) that is translated in greater ease of application.
- Greater quality control, because since human intervention in the process is minimized, the chances of incorrect composition or bad quality of the raw materials decrease.

3.4.3.1 Constitution

Nontraditional gypsum plasters are made with products premixed in factory, made mostly with fine gypsum, eventually slaked lime in powder, mineral aggregates, admixtures and sometimes additions (such as fibres and lightweight fillers). They come to the working site in powder bags to which only the mixing water recommended by the manufacturer must be added. Some of the products can be applied by spraying and others are applied manually (Figs. 3.17 and 3.18). According to BS 5492: 1990 (*internal plastering*), the application by spraying has advantages to coat big areas as long as planning ensures work continuity, since it increases the rate of application and reduces the labour needed.

As for synthetic plasters, also called synthetic binder thin coatings due to their thickness (1–3 mm), they are made with products marketed as ready-to-apply pastes, made essentially of synthetic resins in water dispersions (binder), which are mixed with fillers, normally of silica or calcite, various admixtures and, when necessary or intended, with pigments and extra water.

Premixed gypsum plasters are usually applied in two coats—smoothing coat (10–20 mm), applied generally by mechanical projection, and finishing coat (1–3 mm) applied manually. In general terms, they are made with similar composition products, the main difference being that the first coat is made with coarser materials and is thicker whilst the finishing coat is made of finer materials and is applied over

Fig. 3.17 Manual execution procedure of nontraditional gypsum plasters [26]

Fig. 3.18 Execution and spraying procedure of nontraditional gypsum plasters [26]

Table 3.5 Most adequate pigments to be used in gypsum plasters' composition [28]

White pigments	Rose pigments
– Lithopone, zinc white, titanium dioxide	– Black with weak colouring capacity
Black pigments	Yellow pigments
– Black of natural or artificial irons, with high Fe_2O_3 content, black of magnesium	– Mixture of yellow ochre and sienna earth, chromium, zinc, cadmium, antimony yellow-of-Paris (based on lead oxide)
Grey pigments	Cream pigments
– Black with weak colouring capacity	– Very small amount of yellow ochre
Red pigments	Orange pigments
– Iron oxides with high Fe_2O_3 content (red ochre), artificial iron oxides, calcined sienna iron	– Red iron oxides, natural or artificial, with yellow iron oxides and yellow ochre

the previous one in a very thin layer, almost a pellicle. However, in some cases, these coats can be made with exactly the same product [27].

The products used to make the smoothing and finishing coats are marketed in powder, in *Kraft* paper bags, containing a maximum of 40 kg of product and comprising a valve to allow filling them by injection and automatic zipping with specific equipment. They are generally white or grey (the natural colours of gypsum used as raw material). For non-painted coatings, the product for the finishing coat may incorporate pigments of various light colours (Table 3.5). The bags must contain the following information: commercial designation and reference of the product, name of the manufacturer, colour reference (for pigmented products), amount of product, validity, CE marking (compulsory requirement), reference of the manufacturing lot and, if it is homologated, identification of the corresponding homologation/application document [27].

3.4.3.2 Application On-Site

According to [10], the application of a coating and its drying must be adequately programmed and coordinated with the other works from the same building site, in order to prevent stains and other types of premature degradation of the coated surfaces. It is advisable, on the one hand, that during the application and drying period, the entry of smoke or dirt capable of producing stains is limited and, on the other hand, that the coating's application is preceded by the creation of minimal conditions of protection against prolonged exposure to rain, at least in the seasons where that is justified, to prevent damp stains and/or the softening of the coating (even though reversible).

On site, the products must be stored in their original packaging in closed spaces, with no humidity and reasonably ventilated. However, even under normal storing conditions, the products generally undergo some changes, namely, in terms of setting and hardening, and therefore, it is advised not to use them more than 6 months after they are manufactured. Furthermore, coatings of this type cannot be applied after the paste has started setting, i.e. between 35 min and 1 h and 50 min for products used in the smoothing coat and between 2 h and 10 min and 2 h and

50 min for products used in the finishing coat. The application equipment and tools must be washed with water, whenever work is interrupted [10].

The nature and characteristics of the substrate must be defined and adequately defined by whoever prescribes a coating system. Coatings can be applied directly over most materials that constitute the interior surfaces of the walls and ceilings, namely, concrete cast on-site, non-rendered masonries of fired clay, current aggregate concrete blocks, natural stone, expanded clay concrete blocks and in some cases aerated cellular concrete blocks. In the case of ceilings, nontraditional gypsum coatings may be used on cast concrete slabs or prestressed concrete joint beam slabs with ceramic or concrete lightweight elements [10]. Depending on the substrate chosen, with direct influence on the levels of adherence and quality of the coatings, a set of issues will have to be complied with. As a general character indication of the requirements to be complied with at the application phase of coatings on-site, the following ones are highlighted [10, 13]:

- The coating works cannot start before the corresponding substrates have undergone the most significant part of their initial drying shrinkage (the minimum period of time between the execution of the wall and the application of the coating must vary between 4 and 6 weeks, according to the substrate's material and the weather conditions on-site).
- When the coating is applied, the substrates must have good cohesion, stability and be free of materials that may jeopardize the coating's proper adherence, such as friable or powdery products and oils; special precautions must be taken in the case of precast concrete substrates.
- The substrates must be exempted of environmental humidity; however, if the weather conditions are hot and dry or if the substrate is too absorbent, it is recommended that it is lightly dampened before the coating is applied.
- In very absorbent substrates (main cause of the formation of "ghosts" due to distinct absorption degrees of the substrate's materials), it is recommended that a primary coat that regulates water absorption is applied, made of polymeric dispersion with great alkaline stability.
- So that the maximum thickness admissible of the coating is not exceeded, the substrate must be quite plane: the protrusions whose height is higher than one third of the average thickness of the coating must be adequately trimmed; likewise, recessions greater than 10 mm must be adequately filled with gypsum mass or when they are over 20 mm deep through filling made of brick chips embedded in gypsum mass.
- In the case of excessively smooth or compact surfaces, they must be subjected to a previous preparation by applying an adherence promoter made of a polymeric dispersion without fillers or by chipping the surface, in order to create the needed adherence conditions.
- The smoothing coat must only be applied after a period of time of about 1 month after the walls are executed, after the bedding mortars of the bricks or concrete blocks have undergone most of their initial drying shrinkage; the application is usually made with a single coat, applied directly over the non-rendered masonry

Fig. 3.19 Mechanical treatment of the substrate, eliminating warping and filling cavities with gypsum paste [25]

Fig. 3.20 Spraying of the paste in successive horizontal strips [25]

or cast in situ concrete substrate previously treated (Fig. 3.19), by manual or mechanical projection; in the first case, the paste is spread with a metal trowel, whilst in the second case, it is done through the sprayer mounted on the free tip of a flexible hose connected to the vertical pipe of the spraying device, where the powder is mixed with water; in this situation, the paste must be applied in successive horizontal strips (Fig. 3.20) and later spread and smoothed with a

Fig. 3.21 Smoothing of the current zone with a metal ruler [25]

Fig. 3.22 Smoothing of the salient corners with a corner ruler [25]

metal ruler in the current zone (Fig. 3.21) and with a corner ruler in salient corners (Fig. 3.22); after which the surfaces are checked for planeness (Fig. 3.23); after the paste hardens (about 1 h later), the coating must be smoothed with a different trowel (Fig. 3.24) and squeezed and scratched with a metal trowel to even out the surface (Fig. 3.25) [10, 12, 29, 30].

However, in very irregular surfaces that demand a coating thickness higher than 20 mm, the application of two coats is advised, the first more diluted in order to ease the penetration of the mass in the depressions of the substrate. After its setting

Fig. 3.23 Verticality and horizontality checking of the wall [25]

Fig. 3.24 Levelling the smoothing coat with a trowel [25]

Fig. 3.25 Pressing and scratching of the smoothing coat with a metal trowel [25]

Fig. 3.26 Application of the finishing coat with a trowel [25]

Fig. 3.27 Adjustment of the paste with a trowel in the current zone and salient corners [25]

starts, an indented trowel must be used to increase the surface's roughness and therefore the adherence to the subsequent coat. The second smoothing coat must be applied before the first one dries completely, followed by smoothing of the paste with a ruler and, after it starts to set, by pressing and scratching with a metal trowel, to improve the smoothing and planeness of the surface [10, 30].

The finishing coat must be applied between 4 and 24 h (under normal weather conditions) after the underlying layer is finished, so that the latter has hardened enough and is compatible with the adherence that needs to be mobilized between the two layers. This finishing coat is generally applied manually in a very thin layer, using metal trowels, to ensure the maximum possible smoothness and planeness of the surface (Figs. 3.26, 3.27, and 3.28) [29, 30].

Fig. 3.28 Adjustment of the paste with a corner ruler in re-entrant corners [25]

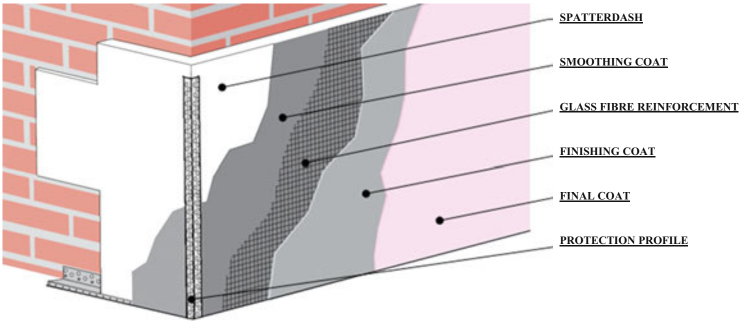


Fig. 3.29 Main protection systems for premixed gypsum plasters (adapted from [31])

There are two main types of protection that are used in premixed gypsum coatings that may be applied over the substrate or be incorporated in their smoothing coat: a metal or glass fibre protection net and metal or perforated PVC profiles (Fig. 3.29). Even though their use is not compulsory, they should be generally prescribed in current situations [27]. The first protection is related to the performance of the substrate under external actions of various natures, such as discontinuities of the substrate or areas of greater concentration of surface stresses, given the geometric heterogeneities of the surfaces (e.g. wall corners, span vertices, slender panels, shutters). If cracking can result from these actions, protection nets should be used, namely, glass fibre (Figs. 3.30 and 3.31). The spacing adopted in these nets should be around 5 mm × 5 mm (depending on the texture and stiffness of the substrate and on the coating to be applied), treated chemically against alkalis.

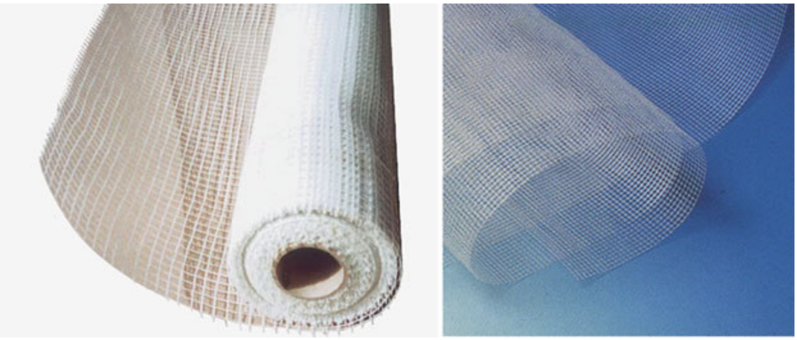


Fig. 3.30 Glass fibre nets used as coating's reinforcement [31, 32]

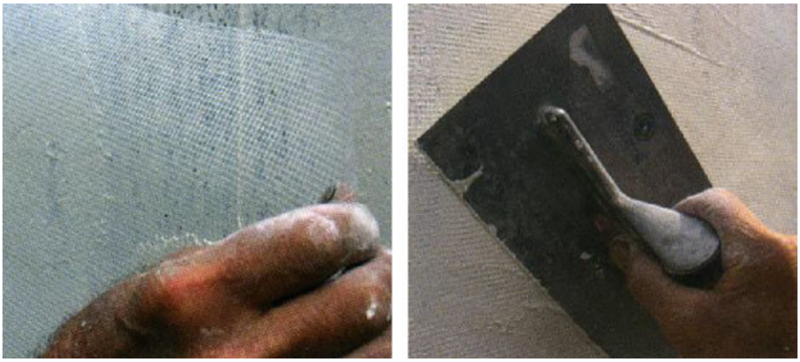
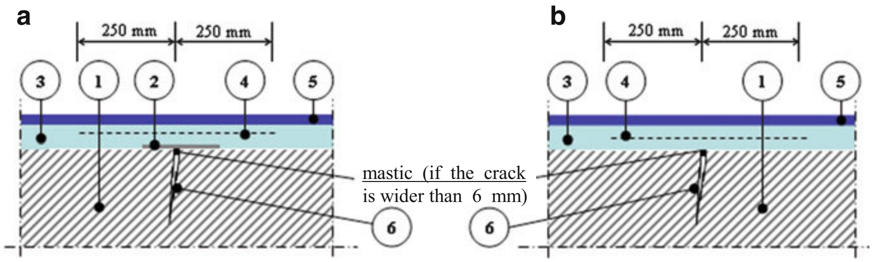


Fig. 3.31 Incorporation of a glass fibre net in the smoothing coat [32]

This protection is particularly important, since the alkalis of cement and other materials that are usually part of the composition of the walls attack the glass fibres, reducing their mechanical strength and elasticity over time [27].

The reinforcement can be applied over the whole coating's area or locally, in areas particularly susceptible to cracking or shock. The fundamental goal of applying the nets is to improve the cracking performance of the coating, increasing its tensile strength, its rupture energy and its capacity to even stresses. The use of a glass fibre net (or a similar one) may thus be recommended in some situations, namely (adapted from [33]):

- Finishing coats applied over others with unknown mechanical behaviour or generally when the coating surface must be crack-free.
- Substrate areas with surface cracking; even though the cracks may be thin, any change of this width causes considerable local stresses in any adhering coating; to increase its capacity to withstand stresses in these areas, the coating must be reinforced with a glass fibre net protected against alkalis, incorporated in the

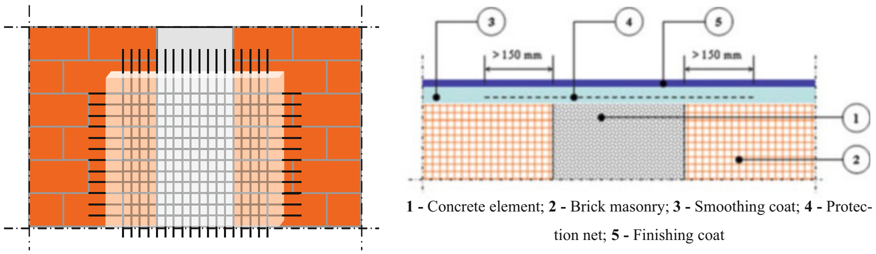


1 - Substrate; **2** - *Kraft* paper or polyethylene leaf; **3** - Smoothing coat; **4** - Protection net; **5** - Finishing coat

Fig. 3.32 Reinforced coating over crack, (**a**) with or (**b**) without a bridge sheet (adapted from [33])

smoothing coat (or in the single coat, in the case of one-coat coatings), which must go beyond both sides of the crack by at least 250 mm (Fig. 3.32).

- Substrate areas made of different materials with a continuous coating (connections masonry-structure), where the distinct thermal expansion coefficients and unequal loading states and deformation moduli tend to cause differential displacements due to the shear stresses that arise in the material's interface. In Portugal, this type of anomaly is found mainly in the frequent case of infilling brick masonry walls contoured by a concrete structure, forming a heterogeneous substrate with a continuous coating. To prevent anomalies of these surfaces, the coating must be reinforced with a glass fibre net protected against alkalis, incorporated in the smoothing coat (or in the single coat, in the case of one-coat coatings), which must go beyond both sides of the joint by at least 150 mm (Fig. 3.33)—this measure is more efficient if the coating is desolidarized from the substrate in the vicinity of the joint, by interposing a strip of thin, elastic and non-putrescible material, such as a strip of unwoven polyester [33, 34].
- Corners of windows/doors or other openings which are locations where stresses concentrate (Fig. 3.34); to prevent cracking due to differential displacements of coating/substrate (particularly significant in stiffer coatings), corner



1 - Concrete element; **2** - Brick masonry; **3** - Smoothing coat; **4** - Protection net; **5** - Finishing coat

Fig. 3.33 Layout of the reinforcement to be used in the transition between different materials (adapted from [33, 35])

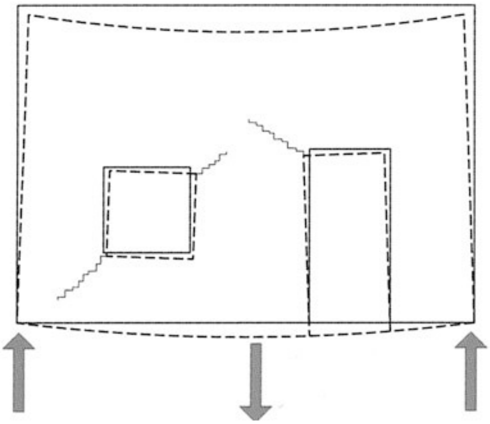


Fig. 3.34 Cracking resulting from stress concentration in openings [35]

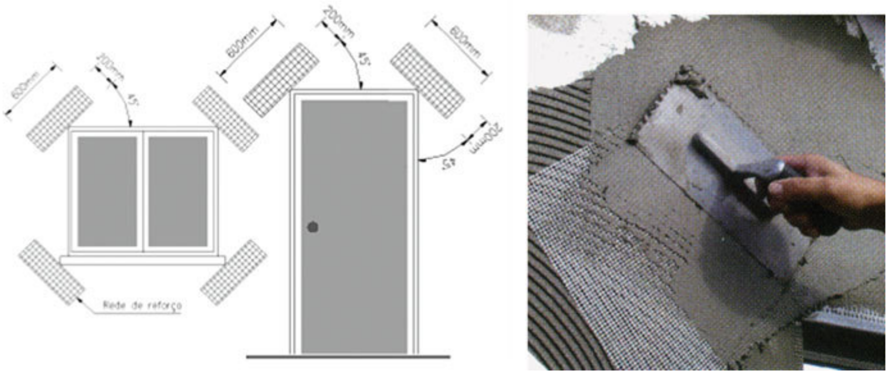


Fig. 3.35 Application of reinforcement in the corners of windows/doors or other openings (adapted from [32, 33])

reinforcements must be used, e.g. glass fibre net with alkali protection or metal net protected against corrosion; the reinforcement net must be applied at 45° and with the size shown in Fig. 3.35.

- Very deformable substrate areas, such as expansion joints; the coatings must be interrupted over every joint in the substrate.
- Areas where localized fillings are needed, using thicker render coats than in the adjoining areas.

The second general protection measure consists of the use of metal protection profiles protected against corrosion (Figs. 3.36 and 3.37) or perforated PVC profiles (more currently used) (Figs. 3.38 and 3.39), in the salient corners of the coating. The objective of using these elements is to increase the local resistance to shock in the coating areas that are more fragile (edges, wall corners or spans) due to their

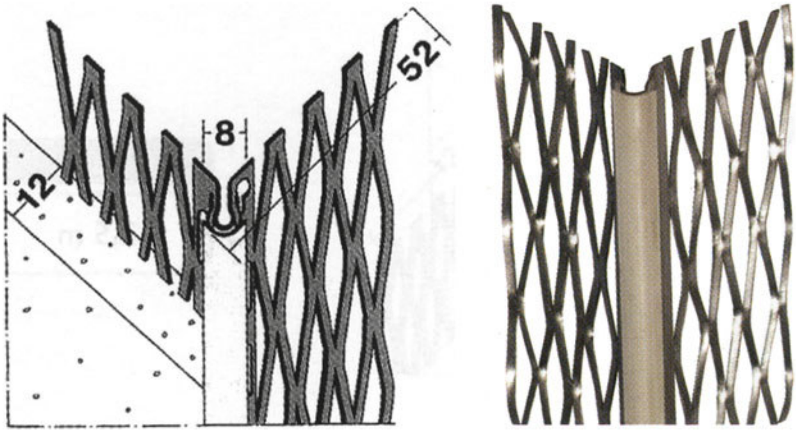


Fig. 3.36 Metal protection profile coated with PVC [31]

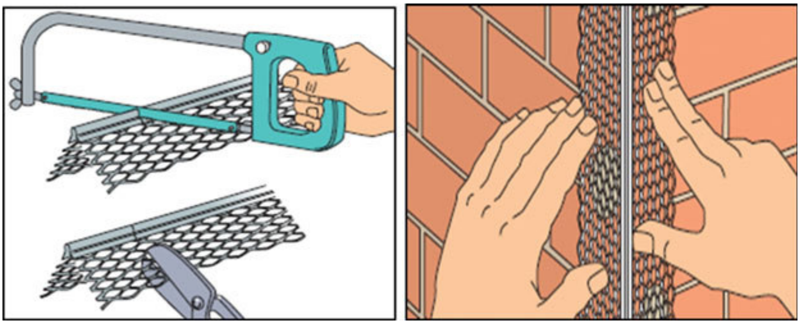


Fig. 3.37 Application of a protection profile in a salient edge of a surface [36]

location or that are subjected to physical aggressions (in circulation areas), but they also contribute to guaranteeing the straightness of these areas [27].

Besides the corner protection profiles, it is equally recommended to apply galvanized steel malleable protection profiles in arch-shaped elements (Fig. 3.40), as well as protection profiles in galvanized steel coated with PVC or simply in PVC (more frequent) in the extreme areas of the coating, in order to increase the resistance of these areas against shocks and abrasion (Fig. 3.41).

In very deformable substrate areas, such as expansion joints, coatings should have a joint too. It is advised to apply a profile made of a glass fibre net with elastic central sections (a flexible membrane or PVC) in order to absorb the movements of the substrate's expansion joint and thus reduce the risk of surface cracking (Figs. 3.42 and 3.43) [27].

Even before the application, the powder product to make the smoothing and finishing coats is mixed with clean water, in the proportion recommended by the manufacturer. Mixing can be manual (Fig. 3.44) or mechanical (Fig. 3.45), using an

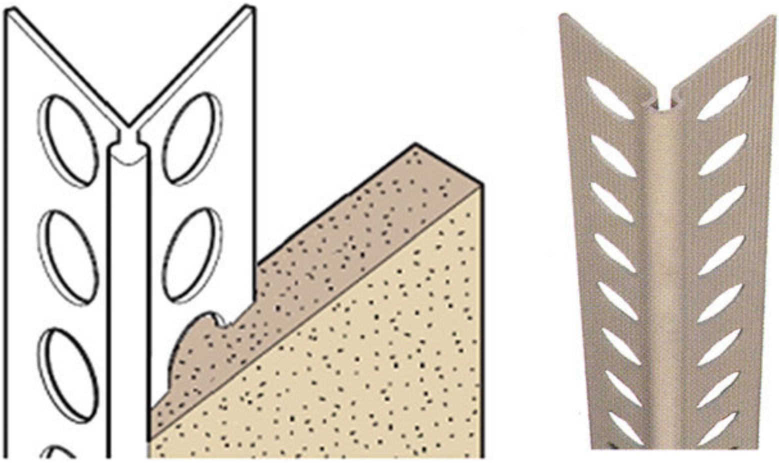


Fig. 3.38 Perforated PVD protection profile [31, 36]

Fig. 3.39 Application of a perforated PVC protection profile in a salient corner of a wall [35]

electric mixer, and it must last until the paste is completely homogeneous. In order to project the coating, mixing is made automatically by the spraying device (Fig. 3.46).

The spraying devices must be recommended by the product's manufacturers. The powder is transported along a tube in which it is mechanically mixed with water, fed through a hose and set by a rotation device in adequate proportion (Fig. 3.47). After the plaster components are mixed by the spraying machine in the required proportions, the paste is then sprayed against the surface. The applier should make sure the paste is applied in successive strips (Fig. 3.48) [27].

The tail ends between different planes are normally made through grooves or covings (Figs. 3.49 and 3.50). Covings, made in situ or prefabricated, must be made of a gypsum-based material or polyurethane, with colour similar to that of the finishing coat, in order to prevent significant colour differences after the paint is

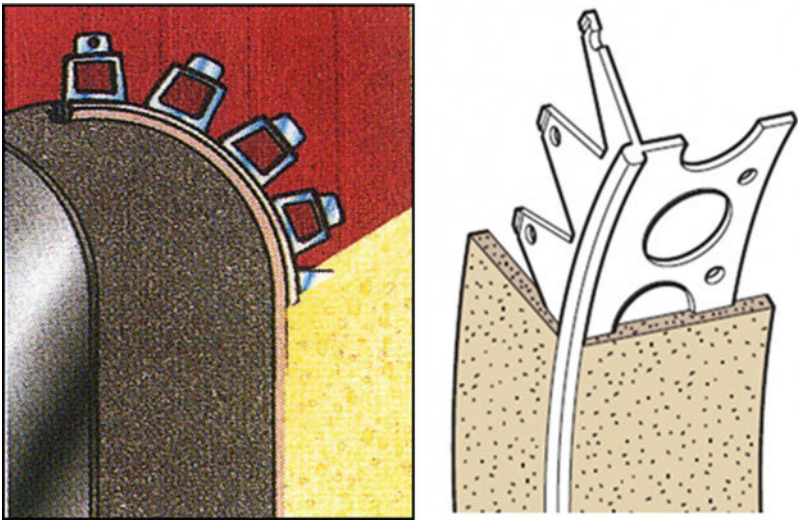


Fig. 3.40 Galvanized steel malleable protection profile for arch-shaped elements [31, 36]

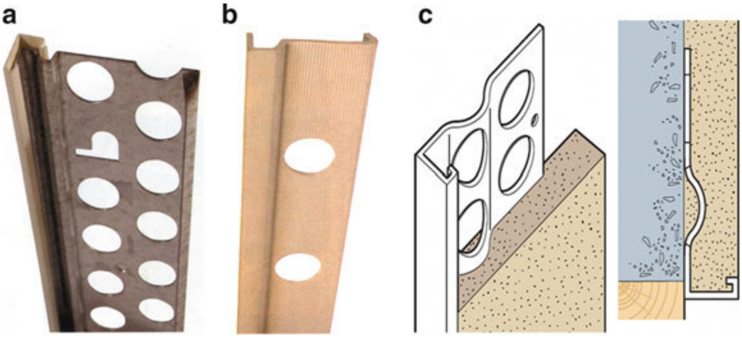


Fig. 3.41 (**a**) Coated galvanized steel protection profile; (**b**) PVC protection profile; (**c**) relative position of the protection profile within the coating [31, 36]

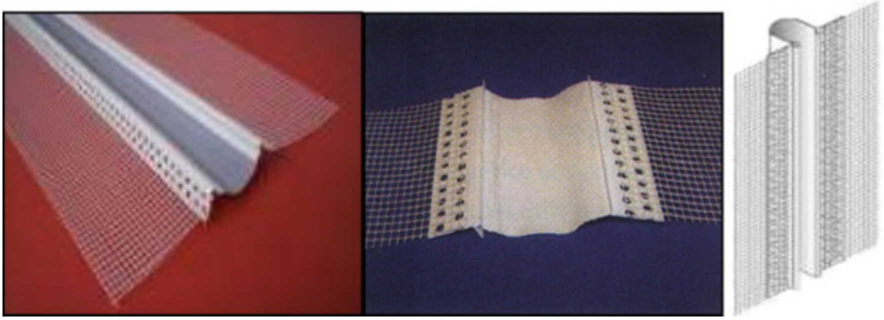


Fig. 3.42 PVC expansion joint profile with net and flexible membrane to match the substrate's expansion joints [32, 37]

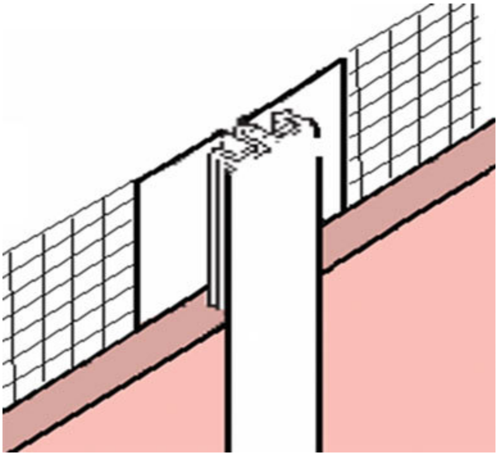


Fig. 3.43 PVC expansion joint profile with net [36]

Fig. 3.44 Mixing with a double spiral mixer [31]

Fig. 3.45 Mixing with an electric mixer [35, 38]

Fig. 3.46 Mixing with the spraying device itself [39, 40]

Fig. 3.47 (**a**) Spraying hose; (**b**) spraying lance with rotation device [31]

Fig. 3.48 Examples of coating application using spraying devices [27]

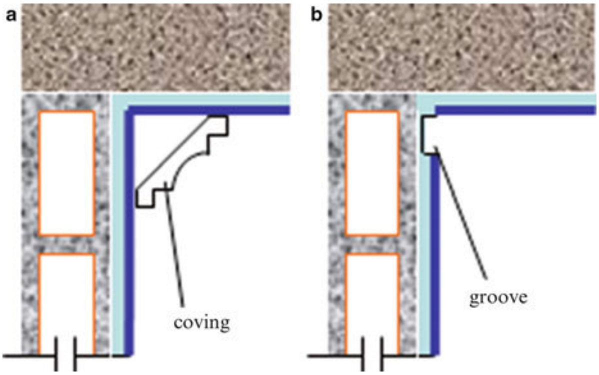


Fig. 3.49 Examples of tail ends of the coating: (**a**) coving; (**b**) groove [27]

Fig. 3.50 Tail end made with a: (**a**) gypsum decorative element (coving); (**b**) groove [27]

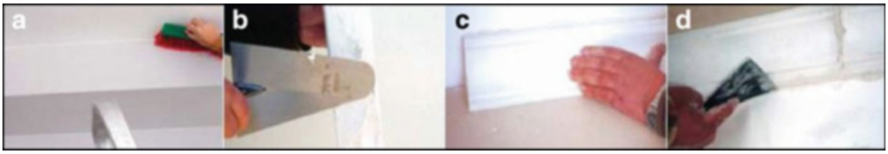


Fig. 3.51 Execution detail of a coving: (**a**) cleaning the substrate; (**b**) applying the gypsum, gluing over the decorative element with a trowel or a spoon; (**c**) manual pressing and slight movement of the piece in order to guarantee a good bond between the coving and the substrate; (**d**) elimination of the excess material and smoothing of the surface with a trowel [31]

applied (Fig. 3.51). The grooves are made of a recession in the plaster's plane, made deliberately with a plated wooden set square, to create a shading area that hides eventual cracks [12].

3.5 Pathology and Diagnosis

3.5.1 Classification of the Anomalies

The nonstructural anomalies of building processes may have the most diverse shapes related to the building areas affected and the functions that are affected, as well as to the materials' nature and construction techniques used and, finally, to the origin, causes and occurrence period of the anomalies [41]. As long as their good quality is demonstrated by a homologation/application document, surfaces coated with nontraditional gypsum plasters minimize the occurrence of anomalies. Nevertheless, the anomalies with the highest probability can be classified in three groups, related to the aggressive agents to which these elements may be subjected, namely, phenomena of physical, chemical and mechanical nature.

Broadly speaking, the most current anomalies are of physical nature, mostly dirt and damp, with emphasis on the latter, since it is one of the most damaging actions that affect current buildings and CIGP as well. Its destructive power is intimately

Table 3.6 Proposed anomalies classification [27]

Code	Defect
D-P	Physical nature
D-P1	Excessive damp
D-P2	Dirt
D-C	Chemical nature
D-C1	Biodeterioration
D-C2	Efflorescence/cryptoflorescence
D-C3.1	Adhesion failure—debonding
D-C3.2	Adhesion failure—bulging
D-C3.3	Adhesion failure—detachment
D-M	Mechanical nature
D-M1.1	Cracking—superficial/irregular
D-M1.2	Cracking—average
D-M1.3	Cracking—linear and deep
D-M2	Impact and other mechanical actions
D-M3	Loss of cohesion/disaggregation

related to gypsum plaster typically having a structure with high open porosity and hygroscopicity that favour water percolation through its microstructure, thus promoting the development of aggressions of various natures: physical (through changing the inter-crystalline adherence of gypsum); chemical (through reactions resulting from the presence of soluble salts in the substrates and the coating itself); and biological (through the development of fungi and moulds). Consequently, the habitability and durability conditions of the housing are strongly affected by the unhealthy conditions created by these anomalies and in a limited number of cases by the fact that these degradations are irreversible and cripple the chances of recovery and reuse of the coatings, making their short-term replacement unavoidable.

The second group of anomalies comprises those that result from chemical phenomena, with emphasis on actions whose manifestations are the development of fungi and bacteria on the plastered surface—biodeterioration; actions that lead to volumetric expansions following the crystallization of existing salts, both in the coating itself and in the substrate, which manifest themselves in the shape of efflorescence and cryptoflorescence; and actions related with the loss of adherence of the coating to the substrate, in the shape of debonding, bulging and detachments.

From the last but equally relevant anomaly group, the phenomena of mechanical nature stand out, namely, dimensional changes of the substrates responsible for cracking of various types, shocks and impacts on the coating's surface and, finally, loss of cohesion/disaggregation of the CIGP. Table 3.6 presents the three groups referred above subdivided in anomalies characteristic of each aggression the coating may be subjected to. This classification, as well as the one presented further on for anomalies causes and diagnosis and rehabilitation techniques, designed mostly for premixed gypsum plasters, is valid practically with no changes for traditional gypsum plasters. Nevertheless, references [6] and [8] might prove interesting to further study the pathology and diagnosis of ancient gypsum plasters.

3.5.2 Classification of the Causes Associated with the Anomalies

An anomaly does not occur isolated, i.e. almost always; it results from the conjunction of various adverse factors that, occurring simultaneously or arising in the sequence of the accumulation of effects, cause or intensify the degradation process of CIGP. To choose the most correct action, know the risks to which plasters may be exposed and efficiently control the development of their anomalies; it is important to correlate the exhaustive knowledge of their symptoms with the global understanding of the causes that foster their advent.

The detailed appraisal of causes is an essential factor to determine the intervention strategies and the solutions to implement in CIGP. However, it is difficult to define the types of their causes in a unique and coherent manner. This difficulty results, among others, from the following aspects (adapted from [41]):

- The great variety of coating materials
- The great complexity of the environment that surrounds the building and the diversity of types of its users' possible actions
- The various phases that a building goes through, including design, project, construction, use, changes of use, maintenance, rehabilitation and demolition
- The frequent and simultaneous intermingling between causes and effects of the various phenomena that may develop, which creates situations in which the same happening may be the consequence of one or more phenomena
- The strong influence of the human factor, by action or lack of it, at the various stages of the degradation process

Bearing in mind these difficulties, the goal here is not to describe exhaustively and individually each of the anomalies that trigger the various pathological processes but rather typify them according to groups and describe and correlate them when characterizing the various symptoms characteristic of the various anomalies in CIGP. To this purpose, a classification system of causes is proposed based on that defined by the Official College of Architects of Madrid [42], which is made of two main groups: that of the direct or close causes and that of the indirect causes.

Direct causes are the ones that immediately cause the anomalies, namely, external mechanical actions and environmental actions, and can be eliminated through appropriate repair solutions. Environmental actions are one of the most important, responsible for around one third of all anomalies that occur in CIGP, especially when they happen during their application or when they are subjected to unpredicted conditions along their service life. The causes related to environmental actions comprise factors such as solar exposure, ambient pollution (even in interior surfaces), temperature, coating's ageing/wear itself and, with a predominant role, water action—the vehicle for practically every chemical agent, even if in the shape of water vapour. As for external mechanical actions, they can equally condition the performance of CIGP, since they comprise a set of varied causes that are often difficult to predict. These actions are related with objects falling, shocks/vibrations, substrate deformations and mostly stress concentrations generated in the interface coating/substrate, whose severity is related directly with the coating's deformability, its resistance to compression, tension and flexure actions and restrictions to shrinkage deformations imposed by the substrate [27].

Indirect causes are all that require the combination with a direct cause for the pathological process to start, such as human causes at the design/project stage, the on-site execution stage or even the use stage of the building. It is common knowledge that the quality of a project is one of the indispensable requirements to guarantee the global quality of construction. Whilst a good project free of errors, omissions and ambiguities and well organized results to a great extent in a guarantee of success in implementing an enterprise, a deficient project may have unpredictable consequence in its development.

Presently, design deficiencies are one of the most significant causes of problems and conflicts in the construction sector, due to inadequacy of the materials specified or inefficiency of the solutions proposed. To demonstrate this case, the set of results of Pereira [27] from a field programme in Portugal scoping a total of 87 CIGP inspected is presented (Figs. 3.52 and 3.53).

Concerning the causes related to design errors, they represent around 26 % of all causes of anomalies in CIGP identified in the sample. Looking at Fig. 3.53, it is concluded that cause C-P1—deficient application of the codes and homologation/application documents—is the most frequent within the group, as a consequence of unawareness or carelessness of the designer concerning the characteristics and limitations of the materials, as well as of the requirements of the various coating systems. Causes C-P2, faulty design/detailing of the ventilation systems; C-P3, faulty design/detailing of the waterproofing systems; and C-P7, faulty design/detailing of the protection systems against mechanical actions, also have a high relative frequency, since the occurrence of any of these causes fosters the emergence of more than one anomaly in CIGP. Cause C-P8—faulty design/detailing of expansion joints, one of the least frequent causes—was identified in only 4.8 % of the cases when the inspections were made [27].

Table 3.7 presents a classification of the causes described above, sorted chronologically in each of the groups proposed. As an example, in group C–E, execution

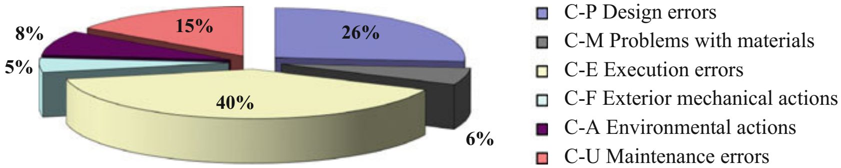


Fig. 3.52 Relative contribution of each group of causes to the occurrence of anomalies in CIGP [27]

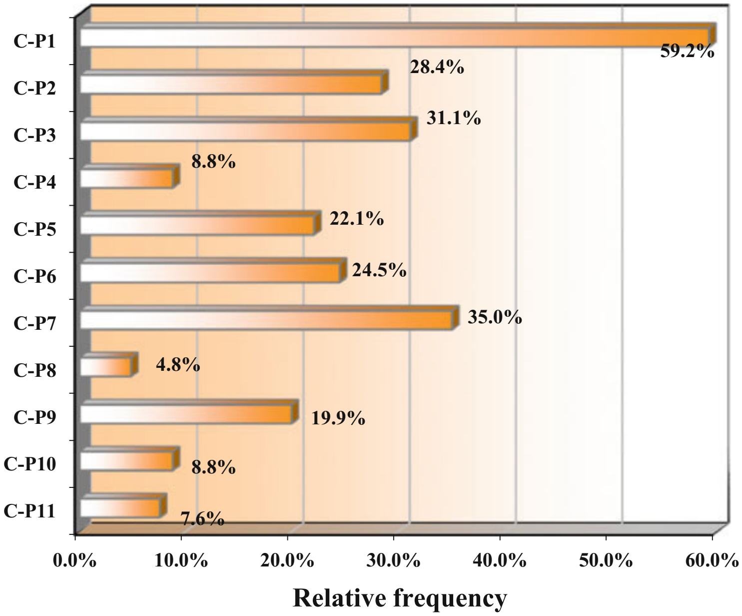


Fig. 3.53 Relative frequency of the design errors identified in 331 anomalies in CIGP (caption in Table 3.7) [27]

errors, the factors related with the preparation of the substrate come before those related with the application and drying conditions of the CIGP.

3.5.3 Classification of the Diagnostic Methods

To plan and fundament any intervention, it is essential in the first place to promote a detailed knowledge, analysis and register of the occurrences. Such action desirably comprises making one or more visits to the site, in order to make the appraisal and represent graphically the types of surface, the materials and the stereotomy of the construction, as well as the analysis of the type of chemical and mechanical actions to which the coating is subjected.

During the site visit, the inspector must try to get in touch with the dwellers that know well the intervention site and collect the greatest number of data on the recent evolution of the anomalies under analysis, on important events that may have influenced or triggered this evolution and on interventions made so far. Further information must be gathered such as photographic registers of the damage and its surroundings and even of other elements that even though not directly related with the anomalies observed may be of interest in future studies [43]. Even though photographic registers, careful observation, a trained eye and a meticulous spirit are the most important and indispensable instruments for such characterization, it is fundamental that the technician in charge of a given intervention resorts to other

Table 3.7 Proposed classification of the causes associated with anomalies in CIGP [27]

Code	Probable cause
C-P	Design errors
C-P1	Deficient application of the codes and homologation/application documents
C-P2	Incorrect design/detailing of ventilation system
C-P3	Incorrect design/detailing of waterproofing system
C-P4	Incorrect design/detailing of water drainage system
C-P5	Malpractice in the definition of structural deformations of the building and their influence on the substrate
C-P6	Negligence in the conditions demanded of the substrate
C-P7	Incorrect design/detailing of the system of protection against mechanical actions
C-P8	Incorrect design/detailing of joints
C-P9	Incorrect prescription of materials
C-P10	Insufficient/absent prescription of tests or execution methods
C-P11	Incorrect prescription of the thickness of IGP layers
C-M	Problems with materials
C-M1	Use of material with production defects
C-M2	Use of nonprescribed, incorrect and/or incompatible materials
C-E	Execution errors
C-E1	Insufficient understanding of the execution project
C-E2	Inexperienced or unskilled gypsum plaster workers
C-E3	Incorrect/absent installation of drainage system
C-E4	Incorrect/absent installation of waterproofing barriers and protection profiles included in the project
C-E5	Incorrect/absent installation of ventilation system
C-E6	Accumulation of mortar debris or other construction waste in air gaps of double walls
C-E7	Incorrect/non-execution of joints
C-E8	Disregard of instructions on mixing quantities and procedures
C-E9	Absent/insufficient mechanical preparation of substrate
C-E10	Inadequate roughness of the substrate
C-E11	Insufficient wetting of the substrate
C-E12	Excessive waterproofing of the substrate
C-E13	Application to dirty, powdery or uneven substrates
C-E14	Lack of application of primer to the support (or insufficient quantity applied)
C-E15	Incorrect/non-installation of protection systems in the interface between different materials
C-E16	Lack of protection on protruding corners particularly exposed to impact
C-E17	Application in damp/rainy weather or uncontrolled dew point
C-E18	Non-compliance with the setting time between the various stages of execution
C-E19	Inadequate depth of the coating
C-E20	IGP with insufficient permeability to water vapour
C-E21	IGP with excessive permeability to water vapour (excessive porosity)
C-E22	Application of inappropriate paint
C-E23	Insufficient supervision/quality control
C-E24	Too short execution time

(continued)

Table 3.7 (continued)

Code	Probable cause
C-F	Exterior mechanical actions
C-F1	Impact/mechanical vibration
C-F2	Differential movement of adjacent materials
C-F3	Excessive stress concentration in the substrate
C-F4	Excessive shrinkage of the IGP
C-A	Environmental actions
C-A1	Solar radiation
C-A2	Extreme temperatures
C-A3	Air pollution
C-A4	Excessive humidity
C-A5	Chemical/biological attack
C-A6	Natural ageing
C-U	Use and maintenance errors
C-U1	Insufficient ventilation
C-U2	Lack of conservation/maintenance works
C-U3	Excessive/incorrect cleaning of IGP
C-U4	Change of the original field of application of the IGP
C-U5	Impact or friction actions related to use, occupation or circulation of the inhabitants
C-U6	Pipe rupture or water penetration

means of diagnosis to obtain more detailed and quantitative data on the anomalies under analysis.

On the one hand, the opinion and training of the inspector on the intervention may vary a lot, and on the other hand, there is a possibility that errors may occur in the evaluation of the real state of the deeper coating layers (namely, the state of its substrate), since they are not visible during the inspection. The complementary means needed are generally tests, both in situ and in the lab, on samples extracted on-site, in locations judiciously chosen and carefully conditioned and transported [22, 44].

In most occurrences, the use of laboratory tests is infrequent, mostly because of the relative complexity of their execution, the time consumed in obtaining some of the results, the sample's characteristics (generally without adequate shapes and sometimes friable and delicate in handling) and the high cost inherent to these tests.

Therefore, and in order to generalize their use, preferably in all construction sites, in situ detection and characterization techniques are privileged, with the least complexity, the least destructive possible and with an efficient, clean and less onerous procedure. In this context, visual observation and on-site experience assume a decisive importance in the interpretation of the results [45]. According to Veiga et al. [22], test methods with these characteristics are still the object of studies all over Europe and far from being consensual.

Table 3.8 Proposed classification of diagnostic methods for CIGP [27]

Code	Diagnostic method
T-A	Temperature
T-A1	Temperature measurement (superficial and/or environmental)
T-B	Water content
T-B1	Damp measurement (superficial and/or environmental—humidity)
T-B2	Measurement of interior damp
T-C	Permeability/porosity
T-C1	Test of water absorption under low pressure
T-D	Salt identification
T-D1	Salt identification
T-E	Cracking
T-E1	Measurement and surveillance of cracks and fissures
T-F	Internal strength
T-F1	Micro-perforation test
T-G	Superficial strength and cohesion
T-G1	Sphere impact
T-G2	Grid cutting test
T-G3	Scratch test
T-G4	Friction test
T-G5	Pendulum sclerometer test
T-H	Resistance to stain formation
T-H1	Assessment of resistance to staining
T-I	Assessment of adhesion to the substrate
T-I1	Pull-off test
T-J	Detachment areas and discontinuity identification
T-J1	Percussion test
T-J2	Infrared thermography
T-J3	Ultrasound test

The classification system proposed is based on the quality criteria required from a gypsum plaster, i.e. the various types of test (destructive and non-destructive) are grouped as a function of the property or characteristic that is under evaluation. The diagnostic methods associated with the anomalies identified in Table 3.7 are characterized by their complexity and adequacy to each specific situation, namely in what concerns about the materials needed, degree of destructiveness, special needs, advantages and limitations. The system therefore considered only the tests that can be performed in situ, given the drawbacks of the lab tests mentioned before. This approach results from this system intending to select relatively simple and expedient tests to inspect and diagnose anomalies on-site. Table 3.8 presents the methods selected for the system, to which are assigned code designations. This system was conceived for premixed gypsum plaster but is equally generically valid for the traditional ones. The CIGP inspection and diagnosis operations are described in detail in Pereira [27]. Figures 3.54 and 3.55 illustrate two of the diagnostic methods selected.

Fig. 3.54 Micro-drilling test [44]

Fig. 3.55 Grid cutting test [46]

3.6 Maintenance and Rehabilitation

3.6.1 Maintenance Strategies

For CIGP to have adequate performance levels during their service life, at the use stage of the building, it is necessary to make various types of interventions, namely, periodic cleaning, inspections and local repairs [10, 47, 48].

Generically, two maintenance strategies may be considered (Table 3.9): proactive, whose objective is to act before failure, degradation or significant loss of performance capacity of each building element occurs, and reactive (also called corrective or curative), which consists on letting the element degradation mechanism act and intervene after the manifestation of the anomaly and corresponding failure [49].

Cleaning operations, even though often underrated, acquire great importance in maintaining the coating's quality, namely, its aesthetics, and preventing the occurrence of other anomalies, such as the evolution of dirt. Furthermore, the lack of cleaning allows the formation of a dirt skin on the coating's surface that reduces its permeability to water vapour. In fact this situation favours the retention of outside damp and can in the end cause adherence losses (debonding, bulging or detachment) in the CIGP. Current cleaning of the surface depends on their finishing.

Table 3.9 Maintenance strategies for wall coatings (adapted from [49])

Maintenance strategy		Characterization	Advantages (+) and limitations (−)
Proactive	Preventive	Planning, at the design stage, of the interventions, with fixed intervals	(+) Reduction of extra works
			(+) Less interference with the normal use of the building
			(+) Optimization of resources and costs
			(−) Demands an analysis from the design stage, with supporting data and a strict control of what was planned and constant updating
	Predictive	Planning of the inspections at the design stage and, based on the reports produced, definition of the actions to be taken	(+) Greater capacity to detect the need and type of intervention, reducing the number of unexpected anomalies
			(+) Modern technology allows detecting problems earlier than with the means used in the past
			(−) It requires a diagnostic method valid during the inspection, with a correct definition of the state of the element
			(−) Need to optimize inspection costs relatively to consequent repair costs, so that the former are enough to make available the necessary means to make a correct and efficient decision
	Improvement	Improve, at the use stage, the initial characteristics, by modifying some of the elements	(+) Improvement of the initial characteristics of the coating, increasing its service life
			(−) Lack of knowledge concerning the in situ long-term performance of the new materials
			(−) Higher costs
Reactive		Intervention after the anomaly/failure occurs	(+) No need for analysis at the design stage
			(−) Extra general costs, even though in the short-term it may look the contrary
			(±) The minimization of these costs necessarily requires the implementation of technical procedures backed by diagnosis files that allow quick answers to solve the anomalies identified

In painted coatings, it is done by simply wiping the dust in dry conditions or, if necessary, washing with a sponge slightly dampened in plain water or with a small content of neutral liquid soap. However, wet cleaning may also affect the coating, due mostly to the need of the water contacting the CIGP, reducing its service life if ventilation conditions are insufficient and/or cracking is pronounced. Unpainted coatings must be cleaned through light sanding of the stained area. However, these cleaning techniques are efficient only against staining resulting from normal use of housing spaces. If these methods are not sufficient, it is advisable to consult the coating's manufacturers and/or to apply the procedures referred in the literature [10, 29, 50].

Inspection operations must follow an established methodology and be sustained by adequate diagnostic methods on the degradation state of each coating (coating's state, cleaning state, adherence to the substrate, eventual cracking, among other aspects). However, these actions must be extended to the envelope of the coating, in order to detect the occurrence of phenomena that lead to existing or potential anomalies, such as infiltrations or condensations. Therefore, actions are taken to anticipate the anomaly instead of correcting it, i.e. the maintenance should be proactive rather than reactive, resulting in economic gains [45, 47–49, 51, 52].

Local repairs must be preceded by not only inspection and diagnosis actions but also by the analysis and correction of the degradation causes, to prevent their recurrence. These operations prevent the propagation of the anomalies to the remaining coating area and may even improve its quality level, also increasing its service life. As an example, the protection of salient corners with plastic profiles, in areas particularly subjected to shock actions, is referred. According to some homologation/application documents, local repairs of surface coatings may be done using the coating products themselves, after complete removal of the original material from the same areas. However, the techniques adopted must be adequate to each anomaly, and deeper interventions even of different nature may be required [10, 47, 48, 51]. Therefore, to find a stricter correlation between a repair technique and an anomaly, consulting the procedures described by Palha [25] is recommended, since they describe these themes in minute detail.

3.6.2 Classification of the Maintenance/Repair Techniques

Aguiar et al. [41], cited by Cotrim [8], define the concept of rehabilitation as "a whole series of options made in order to recover and benefit a building, making it apt for its present use". Silveira [6] defines repair as an "intervention destined to correct anomalies". In fact, the first concept referred has a wider scope, comprising the second. However, in current buildings, the concepts of rehabilitation and repair are frequently misused as equivalent.

On the other hand, maintenance is defined as all technical and administrative actions taken to guarantee adequate performance levels during the service life (ISO 15686-1). In this context, maintenance includes all the inspection, cleaning, repair and partial replacement actions.

Consolidation is a traditional technique used to correct anomalies manifested either by loss of adherence of the plaster to the substrate or between coats and by loss of cohesion of the materials' microstructure, resulting in the friability of the plaster or its softening due to damp [53]. This difficult technique is applied mostly in situations where it is impossible to remove the materials, as in the rehabilitation of painted surfaces (mural painting or painted ornaments) [8]. The hardening and conservation of the surfaces were works needed at the final stage of interventions in gypsum plaster and were meant to confer an aspect and texture similar to polished stone, as a result of filling its porosity, thus precluding the development of fungi and moulds, allowing however the needed exchanges of water vapour [8].

However, the techniques referred in the previous paragraphs are not usually applied in current gypsum plasters, since their very specific character demands very specialized workmanship, which precludes its use in the present context. Furthermore, these solutions are unfavourable from a techno-economic perspective, because the consolidation process is not more efficient, from a performance viewpoint, than the removal of the degraded area and subsequent reposition of the coating and consolidation is more expensive due to the scarcity of specialized personnel. Likewise, hardening and conservation of the surfaces may be replaced by adequate paint systems that prevent the onset of fungi and moulds. On the other hand, for ancient gypsum plasters, it is always worthwhile to preserve them, given their historical value and the incompatibility problems with new materials used in eventual repairs.

In traditional construction, almost all the gypsum plaster substrates are made of wood, namely, timber and masonry walls (structural walls), partition walls and ceilings. In all of them, the first plaster coat is applied on wood lathing, with a trapezoidal cross-section. Therefore, in these cases it is commonly needed to intervene in various wooden elements (supporting structure and lathing) [6, 8]. In current buildings, substrates are completely different: in ceilings normally the concrete slab and in walls brick masonry (more current in the continent) or concrete blocks (more frequent in Azores) are the most frequent options in Portugal.

In ancient gypsum plasters, it is common to replace partially the coatings and the ornaments in areas with gaps. In the latter case, their reproduction must be made by analysing the composition of the remaining part or documents (photos or the original drawings) that identify the original composition. The coatings used to fill the gaps must comply with a set of requirements, namely, being compatible with the ancient plasters at a functional and aesthetic level. However, in contemporary construction, gypsum plaster has lost its artistic character, i.e. gypsum plaster ornaments, the faking of stone and polychrome plasters are limited to traditional construction. In fact, the methods used in the rehabilitation of these elements, an operation also called reintegration [8], are not considered here. The compatibility of the replacement coating with the original one in current practice is ensured by the application of the same products, which is greatly facilitated because they are premixed products, even though it is advised that they are from the same manufacturer. A homogeneous finishing is ensured by the application of a final paint coat, an option also applied in traditional solutions, as referred by Cotrim [8], but mostly aimed at hiding dirt or biologic or salts stains.

The most correct strategy for an intervention comprises of two stages: the elimination of the cause and the subsequent elimination of the anomalies. However, these two actions are generally difficult to implement simultaneously, thus making it necessary to resort to alternative or complementary strategies, namely, protection against the aggressive elements, improvement of the functional characteristics and hiding the anomalies [54]. In fact, even though it is not the most frequent option before intervening in a CIGP, it is essential to determine the causes of existing anomalies [10, 55] through a logical and systematic process of inspection and diagnosis, as well as ensuring their elimination.

Only the interventions to deal with anomalies in CIGP are considered, as an adaptation of the Silvestre [56] classification: curative repair techniques (r_c), preventive repair techniques (r_p) and maintenance works (m), the latter generally cleaning operations.

Curative repair techniques allow repairing, eliminating or hiding the anomaly but can also comprise rehabilitation interventions (repair of CIGP that includes changing the characteristics or the geometry of the materials used, introducing improvements in the coating's performance) or partial or integral replacement of the CIGP [54, 56].

Preventive repair techniques are interventions that even though not directly dealing with the anomaly are needed to eliminate its causes. These techniques can also correspond to rehabilitation interventions or replacement of parts of the CIGP [56].

Maintenance works are periodic interventions destined to prevent or correct slight degradation of the constructions, so that they reach the end of their service life without loss of performance or at least satisfying minimum quality levels [47, 54].

These techniques were divided in four groups, each of which corresponds to the interventions concerning a specific constituent element of CIGP (R-A, surface of the CIGP, or R-B, finishing coat), the whole coating (R-C, CIGP) or its interface with its substrate (R-D, interface substrate—CIGP).

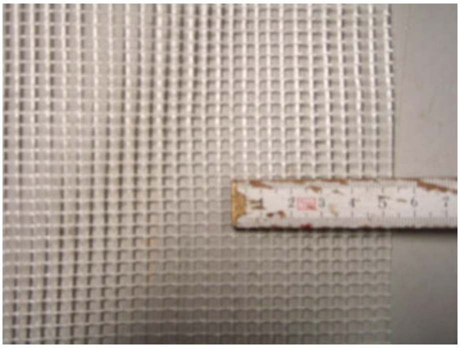
Table 3.10 contains a list of the repair and maintenance techniques that integrate the classification system proposed. It was conceived for premixed gypsum plasters but is also valid for the traditional ones, even though Cotrim [8] presents a more detailed survey for ancient gypsum plasters. The maintenance and repair operations in CIGP are described in detail in Palha [25]. Figures 3.56 and 3.57 illustrate two of the repair techniques selected.

Table 3.10 Proposed classification of the curative (r_c), preventive (r_p) and other maintenance work (m) techniques for CIGP [25]

R-A, surface of the CIGP
R-A1 Cleaning of the CIGP (r_c/m)
R-A2 Application of the fungicide on the surface of the CIGP (r_p/r_c)
R-B, finishing coat
R-B1 Filling of cracks (r_c)
R-B2 Application of a thin finishing coat over the existing CIGP (r_c)
R-C, CIGP
R-C1 Integral/partial replacement of the CIGP (r_c)
R-C2 Incorporation of a net in the smoothing coat of the CIGP (r_c)
R-C3 Protection of salient corners (r_p/r_c)
R-C4 Incorporation of fungicide in the CIGP (r_p/r_c)
R-C5 Removal/replacement of corroded metal elements and gypsum plaster repair (r_p/r_c)
R-C6 Local reinforcement of the CIGP with staples (r_c)
R-D, interface substrate—CIGP
R-D1 Local bridging of the coating (r_c)

Fig. 3.56 Filling a crack with gypsum finish material [25]

Fig. 3.57 Incorporation of a glass fibre net [25]



3.7 Standardization

Gypsum plasters are presently regulated by standards EN 13279-1: 2008, relative to the definitions and requirements of gypsum and gypsum-based coatings, and EN 13279-2: 2004, which deals with the test methods of these coatings. These normative documents from CEN (*Comité Européen de Normalisation*) are the basis for CE marking, referred in the Construction Products Regulation (CPR, N. 305/2011) that replaces the Construction Products Directive (CPD, 89/106/EEC), which allows the free circulation of products in the market within the European economic space.

Before the approval of standard EN 13279, gypsum-based coatings were covered by the European and national standards, namely, France and the United Kingdom. The French standardization include the *Document Technique Unifié* (DTU) 25.1—relative to interior gypsum coatings—standards NF B 12-300, NF B 12-301, NF B 12-303 and NF B12-401, which establish the general conditions for packaging, delivery and reception and define the technical classifications and test specifications for gypsum coating products. In the United Kingdom, these coatings were treated in standards BS 5492: 1990, which deal with interior coatings; BS 1191-1: 1973 and BS 1191-2: 1973, relative to the specification for gypsum building plasters and premixed lightweight plasters. Presently some standards have been withdrawn, and other national documents (e.g. technical specifications) lost their normative nature, even though they provide many relevant data for this type of coating, often including a larger and more focused set of requirements than standard EN 13279, for some quality parameters.

Gypsum for construction, the main constituent of gypsum plasters, is the object of various standards. The lists of selected references in Tables 3.11 and 3.12 present standards and codes relative to gypsum plaster (or gypsum). These references are not in the general reference list at the end of the chapter.

Final Note

This chapter, dedicated to gypsum plasters applied on walls and ceilings' interior surfaces, was based mostly on two Master Dissertations on Civil Engineering, "Technology and rehabilitation of current interior gypsum plasters" [25] and "Inspection and diagnosis system of current interior gypsum plasters" [27], respectively, by Filipe Palha and Ana Pereira, both of which under the scientific supervision of the first author of this chapter. These works also lead to three papers [57–59] in international journals.

Books/Magazines/Journals

- ASTM Manual 67 MNL67 Gypsum: Connecting Science and Technology, Manual/Monograph, Kuntze Richard January 2009MNL67-EB

Table 3.11 ASTM standards related with internal plasters and gypsum-based products

Standard	Year	Title
A641/641M	2009	Specification for zinc-coated (galvanized) carbon steel wire
C11	2013	Terminology relating to gypsum and related building materials and systems
C22/C22M	2010	Specification for gypsum
C28/C28M	2010	Specification for gypsum plasters
C25	2011	Test methods for chemical analysis of limestone, quicklime and hydrated lime
C29/C29M	2009	Test method for bulk density (unit weight) and voids in aggregate
C35	2009	Specification for inorganic aggregates for use in gypsum plaster
C59/C59M	2011	Specification for gypsum casting plaster and gypsum moulding plaster
C61/C61M	2011	Specification for gypsum Keenes cement
C136	2006	Test method for sieve analysis of fine and coarse aggregates
C206	2009	Specification for finishing hydrated lime
C207	2011	Specification for hydrated lime for masonry purposes
C317/C317M	2010	Specification for gypsum concrete
C318/C318M	2013	Specification for gypsum form board
C471M	2012	Test methods for chemical analysis of gypsum and gypsum products (metric)
C472	2009	Test methods for physical testing of gypsum, gypsum plasters and gypsum concrete
C473	2012	Test methods for physical testing of gypsum panel products
C475/C475M	2012	Specification for joint compound and joint tape for finishing gypsum board
C514	2009	Specification for nails for the application of gypsum board
C557	2009	Specification for adhesives for fastening gypsum wallboard to wood framing
C587	2009	Specification for gypsum veneer plaster
C631	2009	Specification for bonding compounds for interior gypsum plastering
C754	2011	Specification for installation of steel framing members to receive screw-attached gypsum panel products
C778	2013	Specification for sand
C841	2013	Specification for installation of interior lathing and furring
C842	2010	Standard specification for application of interior gypsum plaster
C843-99	2012	Standard specification for application of gypsum veneer plaster
C844	2010	Specification for application of gypsum base to receive gypsum veneer plaster
C847	2012	Specification for metal lath
C933	2013	Specification for welded wire lath
C954	2011	Specification for steel drill screws for the application of gypsum panel products or metal plaster bases to steel studs from 0.033 in. (0.84 mm) to 0.112 in. (2.84 mm) in thickness

(continued)

Table 3.11 (continued)

Standard	Year	Title
C955	2011	Specification for load-bearing (transverse and axial) steel studs, runners (tracks) and bracing or bridging for screw application of gypsum panel products and metal plaster bases
C1002	2013	Specification for steel self-piercing tapping screws for the application of gypsum panel products or metal plaster bases to wood studs or steel studs
C1007	2011	Specification for installation of load-bearing (transverse and axial) steel studs and related accessories
C1032	2011	Specification for woven wire plaster base
C1047	2010	Specification for accessories for gypsum wallboard and gypsum veneer base
C1177/1177M	2013	Specification for glass mat gypsum substrate for use as sheathing
C1178/C1178M	2013	Specification for coated glass mat water-resistant gypsum backing panel
C1278/1278M	2011	Specification for fibre-reinforced gypsum panel
C1396/1396M	2013	Specification for gypsum board
C1546	2008	Guide for installation of gypsum products in concealed radiant ceiling heating systems
D75	2009	Practice for sampling aggregates
D1193	2011	Specification for reagent water
D1784	2011	Specification for rigid poly(vinyl chloride) (PVC) compounds and chlorinated poly(vinyl chloride) (CPVC) compounds
D2013	2012	Practice for preparing coal samples for analysis
E84	2013	Test method for surface burning characteristics of building materials
E90	2009	Test method for laboratory measurement of airborne sound transmission loss of building partitions and elements
E96/E96M	2012	Test methods for water vapour transmission of materials
E119	2012	Test methods for fire tests of building construction and materials
E337	2007	Test method for measuring humidity with a psychrometer (the measurement of wet- and dry-bulb temperatures)
E492	2009	Test method for laboratory measurement of impact sound transmission through floor-ceiling assemblies using the tapping machine

- Walls & Ceilings Magazine—http://www.wconline.com/
- Global Gypsum Magazine—http://www.globalgypsum.com/magazine/latest-issue
- Construction and Building Materials
- Journal of Fire Sciences
- Journal of the American Ceramic Society
- Cement and Concrete Research
- Minerals Engineering

Table 3.12 European standards related with internal plasters and gypsum-based products

Standard	Year	Title
EN 520 +A1	2004; 2009	Gypsum plasterboards—Definitions, requirements and test methods
EN 998-1	2010	Specification for mortar for masonry—Part 1: Rendering and plastering mortar
EN 13279-1	2008	Gypsum binders and gypsum plasters—Part 1: Definitions and requirements
EN 13279-2	2004	Gypsum binders and gypsum plasters—Part 2: Test methods
EN 13658-1	2005	Metal lath and beads—Definitions, requirements and test methods—Part 1: Internal plastering
EN 13815	2006	Fibrous gypsum plaster casts—Definitions, requirements and test methods
EN 13914-2	2005	Design, preparation and application of external rendering and internal plastering—Part 2: Design considerations and essential principles for internal plastering
EN 13915	2007	Prefabricated gypsum plasterboard panels with a cellular paperboard core—Definitions, requirements and test methods
EN 13950	2005	Gypsum plasterboard thermal/acoustic insulation composite panels—Definitions, requirements and test methods
EN 13963/AC	2005; 2006	Jointing materials for gypsum plasterboards—Definitions, requirements and test methods
EN 14190	2005	Gypsum plasterboard products from reprocessing—Definitions, requirements and test methods
EN 14195/AC	2005; 2006	Metal framing components for gypsum plasterboard systems—Definitions, requirements and test methods
EN 14209	2005	Preformed plasterboard cornices—Definitions, requirements and test methods
EN 14353 +A1	2007; 2010	Metal beads and feature profiles for use with gypsum plasterboards—Definitions, requirements and test methods
EN 14496	2005	Gypsum-based adhesives for thermal/acoustic insulation composite panels and plasterboards—Definitions, requirements and test methods
EN 14566 +A1	2008; 2009	Mechanical fasteners for gypsum plasterboard systems—Definitions, requirements and test methods
CEN/TR 15123	2005	Design, preparation and application of internal polymer plastering systems
CEN/TR 15124	2005	Design, preparation and application of internal gypsum plastering systems
CEN/TR 15125	2005	Design, preparation and application of internal cement and/or lime plastering systems
EN 15319	2007	General principles of design of fibrous (gypsum) plaster works
EN 15824	2009	Specifications for external renders and internal plasters based on organic binders
CEN/TR 16239	2011	Installation rules of fibrous (gypsum) plaster works

- Materials Structures
- Journal of Environmental Management
- Energy and Buildings

Associations/Organizations/Societies

- The Gypsum Association—http://www.gypsum.org/about/mission/
- American Institute of Building Design—http://www.aibd.org/
- Association of the Wall and Ceiling Industry—http://www.awci.org/
- Ceilings & Interior Systems Construction Association (CISCA)—http://www.cisca.org/i4a/pages/index.cfm?pageid=1
- Drywall Finishing Council—http://www.dwfc.org/
- EPS Molders Association—http://www.epsindustry.org/
- Eurogypsum—http://www.eurogypsum.org/
- European Mortar Industry Organisation—http://www.euromortar.com/home/
- Mortar Industry Association—www.mortar.org.uk
- International Masonry Society—www.masonry.org.uk

Companies/Gypsum Products

- American Gypsum Company LLC—http://americangypsum.com/
- CertainTeed Gypsum Inc.—http://www.certainteed.com/products/gypsum
- Georgia-Pacific Gypsum—http://www.buildgp.com/Georgia-Pacific-Gypsum
- Lafarge North America—http://www.lafarge-na.com/wps/portal/na
- National Gypsum Co.—http://nationalgypsum.com/
- PABCO Gypsum—http://www.pabcogypsum.com/
- United States Gypsum—http://www.usg.com/content/usgcom/en.html

References

1. Malinowski R (1982) Ancient mortars and concretes: aspects of their durability. In: Histoire of technology, 7th annual volume, Mansell, UK, pp 89–101
2. Boynton R (1980) Chemistry and technology of lime and limestone, 2nd edn. Wiley, New York
3. Torraca G (1988) Porous materials building. In: Materials science for architectural conservation (3rd ed). ICCROM, Roma
4. Adam JP (1989) La construction romaine. In: Matériaux et Techniques (2nd éd). Grand Manuel Picard, Paris
5. Vasconcelos F (1991) Decorative gypsum plasters from the North of Portugal (in Portuguese). Calouste Gulbenkian Foundation and Regional Centre of Traditional Arts, Porto
6. Silveira P (2000) Ancient gypsum plasters: building characterization and pathological analysis (in Portuguese). MSc Dissertation in Construction, Instituto Superior Técnico, Lisbon

7. Santos C (2002) João Maria Policarpo May. Designer and teacher of the Drawing Course of the Royal Silk Factory (in Portuguese). Sciences and Techniques of the Heritage, Faculdade de Letras, Porto, pp 203–209
8. Cotrim H (2004) Rehabilitation of ancient gypsum plasters (in Portuguese). MSc Dissertation in Construction, Instituto Superior Técnico, Lisbon
9. Veiga MR (2004) Walls coatings: function and requirements (in Portuguese), LNEC/FUNDEC course: pathology of walls coatings—ways to prevent it. National Laboratory of Civil Engineering, Lisbon
10. LNEC (1995) Specialization course on walls coatings (in Portuguese). Veiga MR (Coordination). National Laboratory of Civil Engineering, Lisbon
11. Vilhena A, Veiga MR (1995) Bases for the homologation of premixed gypsum coatings for walls interior surfaces (in Portuguese). National Laboratory of Civil Engineering, Lisbon
12. Fernandes A (2000) Inspection and test plan for the execution of projected gypsum pastes (in Portuguese). MSc Dissertation in Construction, Instituto Superior Técnico, Lisbon
13. Lucas JC (1990) Functional requirements of walls coatings (in Portuguese). Buildings technical information, ITE 25. National Laboratory of Civil Engineering, Lisbon. ISBN 972-49-1508-5
14. Sabbatini F (2007) Suggestions to conceptualize durability and service life (in Portuguese) Project of performance standard. FHS Consultoria e Engenharia, Sao Paulo
15. Ashurst J, Ashurst N (1989) Mortars, plasters and renders. In: Practical building conservation, vol 3, English heritage technical handbook. Gover Technical, Hants. ISBN 0-291-39747-6
16. Fernandes M (1984) The influence of hydrated lime on the strength of mortars (in Portuguese). Report 275/84 NAB. LNEC, Lisbon
17. Velosa A (2009) Use of pozzolans in mortars for buildings' conservation (in Portuguese). In: Seminar on coating mortars in ancient buildings. ITECONS, Coimbra
18. Lucas JC (1990) Synthetic binders' coatings for walls interior surfaces (in Portuguese). Buildings technical information, ITE 27. National Laboratory of Civil Engineering, Lisbon
19. Gonçalves T (1997) Waterproofing capacity of mineral binders-based wall coatings. Development of a test method based on electric resistance (in Portuguese). MSc Dissertation in Construction, Instituto Superior Técnico, Lisbon
20. Branco JP (1993) Manual of gypsum plasters and modelling (in Portuguese) (2nd ed). Collection "Learn Civil Construction". EPGE, Lisbon
21. Lucas JC (1968) Coatings for walls interior surfaces made of aerated cellular concrete blocks (in Portuguese). Specialist Thesis, National Laboratory of Civil Engineering, Lisbon
22. Veiga MR, Aguiar J, Silva AS, Carvalho F (2004) Conservation and renovation of walls coatings in ancient buildings (in Portuguese). National Laboratory of Civil Engineering, Lisbon. ISBN 972-49-2009-7
23. Branco JP (1981) Mason manual (in Portuguese). National Laboratory of Civil Engineering, Lisbon, p 198. ISBN 972-49-1158-6
24. Segurado J (n.d.) Construction finishing: gypsum plasters, paints, etc. (in Portuguese). Editor Bertrand, Lisbon
25. Palha F (2008) Technology and rehabilitation of current interior gypsum plasters (in Portuguese). MSc Dissertation in Civil Engineering, Instituto Superior Técnico, Lisbon
26. ATEDY (2003) Manual de ejecución de revestimientos interiores con yesos. ATEDY, Madrid
27. Pereira A (2008) Inspection and diagnosis system of current interior gypsum plasters (in Portuguese). MSc Dissertation in Civil Engineering, Instituto Superior Técnico, Lisbon
28. Arredondo F (1980) Estudio de materiales II—El yeso. Instituto Eduardo Torroja de la Construcción y del Cemento, Madrid
29. LNEC (2006) Proyal XXI with Mecafino plus finishing: interior coatings of walls and ceilings (in Portuguese). Application document DA 4. National Laboratory of Civil Engineering, Lisbon

30. LNEC (2007) Proyal with Mecafino Plus finishing: Interior coatings of walls and ceilings (in Portuguese). Application document DA 5. National Laboratory of Civil Engineering, Lisbon
31. Topeca. http://www.topeca.com/. Accessed 11 February 2008
32. Weber (2008) Weber guide, technical catalogue. Weber
33. LNEC (2007) Viplás 50, Viplás 90, Viplás 100, Viplás Mi 167 e Viplás AR 95. Reinforcement nets of walls coatings. Homologation document DH 873. National Laboratory of Civil Engineering, Lisbon
34. Veiga MR (1997) Performance of walls coating mortars: Contribution for the study of their cracking resistance (in Portuguese). PhD Thesis in Civil Engineering, FEUP, Porto. ISBN 972-49-1757-6
35. Secil M (2007) Dry mortars (in Portuguese). Technical catalogue, Lisbon
36. Expamet. Expamet building products. http://www.expamet.co.uk/. Accessed 8 March 2008
37. Suprapainel. http://www.suprapainel.pt/produtos.html/. Accessed 28 February 2008
38. Grabe. Equipment (in Portuguese). http://www.grabe.com.br/. Accesses 8 March 2008
39. Sabbatini F, Franco L, Barros M, Souza U (2004) Walls and ceiling coatings: Gypsum. Transparencies (in Portuguese). Buildings Construction technology II. Department of Civil Construction Engineering, Polytechnic School of the University of São Paulo, São Paulo
40. Supergesso. www.supergesso.com/. Accesses 14 March 2008
41. Aguiar J, Cabrita R, Appleton J (1998) Support guide to the rehabilitation of housing buildings (in Portuguese). National Laboratory of Civil Engineering, Lisbon. ISBN 972-49-1726-6
42. Colegio Oficial de Arquitectos de Madrid (1991) Curso de patología, conservación y restauración de edificios, Tomo 1. Colegio Oficial de Arquitectos de Madrid, Madrid. ISBN 84-7740-040-4
43. Arêde A, Costa A (2005) Structural inspection and diagnosis of historical constructions (in Portuguese). In: The intervention on the heritage—practices of conservation and rehabilitation: second seminar, vol 1. FEUP, General Direction of National Buildings and Monuments, Porto, pp 55–88
44. Veiga MR (2003) Mortars in conservation (in Portuguese). In: First workshop on civil engineering of the Aveiro University, evaluation and rehabilitation of existing constructions, Aveiro
45. Cóias V (2006) Inspections and tests in buildings rehabilitation (in Portuguese). IST Press, Lisbon. ISBN 972-8469-53-5
46. Flores-Colen I, de Brito J, de Freitas V (2009) Expected render performance assessment based on impact resistance *in-situ* determination. Constr Build Mater 23(9):2997–3004
47. Flores-Colen I, de Brito J (2003) The influence of some parameters on the reliability of maintenance strategies in current buildings (in Portuguese). In: 3° ENCORE, meeting on conservation and rehabilitation of buildings. National Laboratory of Civil Engineering, Lisbon, pp 1017–1025
48. Silva V (2004) Practical guide for the conservation of real estate (in Portuguese). State Secretariat of Housing, Editor Dom Quixote, Lisbon
49. Flores I (2002) Maintenance strategies: elements of the envelope of current buildings (in Portuguese). MSc Dissertation in Construction, Instituto Superior Técnico, Lisbon
50. Lucas JC (1990) Classification and general description of walls coatings in masonry and concrete (in Portuguese). Buildings technical information, ITE 24. National Laboratory of Civil Engineering, Lisbon. ISBN 972-49-1507-7
51. Flores-Colen I (2003) Pro-active maintenance plans in recent buildings (in Portuguese). In: 3° ENCORE, meeting on conservation and rehabilitation of buildings. National Laboratory of Civil Engineering, Lisbon, pp 1027–1035
52. Veiga MR (2004) Cracking performance of renders: evaluation and improvement (in Portuguese). In: Coatings in recent buildings (1st ed). National Laboratory of Civil Engineering, Lisbon, pp 7–27. ISBN 972-49-2022-4

53. Aguiar J, Tavares M, Veiga MR (2001) Consolidation of exterior coatings (renders and mortars) of ancient buildings: reflexions on a study plan (in Portuguese). National Laboratory of Civil Engineering, Lisbon
54. Gonçalves A (2007) Rehabilitation of masonry walls (in Portuguese). MSc Dissertation in Construction, Instituto Superior Técnico, Lisbon
55. Appleton J (2003) Rehabilitation of ancient buildings. In: Pathologies and technologies of interventions (in Portuguese) (1st ed), Orion Edições. ISBN 972-8620-03-9
56. Silvestre J (2005) Supporting system to the inspection and diagnosis of anomalies in adhered ceramic claddings (in Portuguese). MSc Dissertation in Construction, Instituto Superior Técnico, Lisbon
57. Pereira A, Palha F, de Brito J, Silvestre J (2011) Inspection and diagnosis system for gypsum plaster in partition walls and ceilings. Constr Build Mater 25(4):2146–2156
58. Palha F, Pereira A, de Brito J, Silvestre J (2012) Effect of water on the degradation of gypsum plaster coatings: inspection, diagnosis and repair. J Perform Constr Facil 26(4):424–432
59. Pereira A, Palha F, de Brito J, Silvestre J (2014) Diagnosis and repair of gypsum plaster coatings: Statistical characterization and lessons learned from a field survey. J Civil Eng Manag accepted for publication 20(4):486–496

Concrete

4

Manuel Vieira

Abstract

Concrete is a composite material of a cement-based matrix, which is produced by mixing water and a binder, usually made of hydraulic cement or cement and additions and particles of aggregate. The resulting product, by mixing those constituents, is very versatile both in terms of the characteristics it can have and the applications it can be used for. This versatility contributes to make concrete the most used construction material in Portugal and most of the world. The production of concrete, especially at construction sites, is not carried out under so controlled conditions as other construction materials, such as steel. Producing good concrete requires a set of precautions to be taken. "Bad" concrete—with inadequate consistence, excess voids and a very heterogeneous structure—is produced using exactly the same constituents as good concrete. The difference is in knowing and understanding the phenomena that govern its behaviour.

Keywords

Concrete • Paste • Mortar • Mix design • Quality control • Production • Performance • Durability • Casting • Compaction • Mixing • Fresh concrete • Hardened concrete • Hydration • Cement

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M.C. Gonçalves, F. Margarido (eds.), *Materials for Construction and Civil Engineering*, DOI 10.1007/978-3-319-08236-3_4

4.1 Concrete with Hydraulic Binders

4.1.1 Introduction

Concrete is a composite material of a cement-based matrix, which is produced by mixing water and a binder, and particles of aggregate.

The binder normally consists of hydraulic cement or cement and additions. The aggregates are granular material, specifically sand and crushed or rounded rock particles. Usually, other components, in smaller amount, known as admixtures, also make part of the concrete, with the aim of improving some characteristics of the concrete. This material, with those constituents, is very versatile both in terms of the characteristics it can have and the applications it can be used for.

This versatility contributes to make concrete the most used construction material in Portugal and most of the world. Among the reasons the use of concrete is so widespread compared with alternative materials such as steel, one can cite the following: its components are economically competitive and available in many different areas of the globe; its application requires little energy, and it has good resistance against both structural and environmental actions; the different structural elements can be moulded easily into different shapes and sizes.

In light of the large number and diverse nature of its components, concrete can have very varied characteristics, which allows it to meet a wide range of requirements. These may be related to the consistency of the concrete, which ranges from dry to very fluid, or its compressive strength, which can range from 0.5 MPa to more than 800 MPa. This wide range of values is difficult to achieve with any other material.

The production of concrete, especially at construction sites, is not carried out under so controlled conditions as other construction materials, such as steel. Producing good concrete requires a set of precautions to be taken. “Bad” concrete—with inadequate consistency, excess voids and a very heterogeneous structure—is produced using exactly the same constituents as good concrete. The difference is in knowing and understanding the phenomena that govern its behaviour.

When asking what makes a good concrete, there are two criteria to consider: concrete should satisfactorily meet, on the one hand, the requirements of mixing, transport and casting while it is fresh and, on the other, the requirements for when it is in its hardened state. When fresh, concrete should have a consistency that allows it to be compacted by the means planned without excessive force, and it should have a composition that is resistant to segregation during transport and laying so that the concrete element is homogeneous throughout. The main requirements of good concrete when hardened are appropriate mechanical strength, deformability and durability [1].

4.1.2 Historical Overview

4.1.2.1 Etymology of the Terms *Concrete* and *Betão*

The word *concrete* has its roots in the Latin word *concretus*, which has the following meanings: hardened, solidified, congealed and clotted. Those are the characteristics of a mouldable material that coalesces.

The Portuguese word *betão* comes from the French word *béton*. It is believed to originate from the Latin *bitumen*, which in France evolved into *betunium* and *betun*, which in Old French meant viscous mud, rubble and dirt. This led to the current name for *betão* because when it is ruined it becomes rubble. On the other hand, the Latin term *bitumen* is naturally the root of the word bitumen, which was used as a binder in construction materials. Nonetheless, bitumen is not a component of concrete, which leads to the theory that its roots lead back to concrete's ability to set. This theory is based on the ancient verb *beter*, of German origin, which is linked to the idea of coagulation and agglomeration, since its derivate *beizen* means a chemical action linked to the coagulation of milk by acids. In light of the uncertainty surrounding the etymology of the term *betão*, the answer lies somewhere among these theories and is linked to concrete's ability to remain agglomerated through the action of a binder [2].

4.1.2.2 Concrete: From Ancient Times to Modernity

The idea of using mixtures of stones and sand with a binder is perhaps as old as mankind itself. The earliest uses have not lasted to the present day, certainly because of the nature of the binder, which was probably clay. One of the oldest examples of concrete was discovered in Lepenski Vir, in what is now Serbia, on the banks of the River Danube, and dates from 5600 BC. It is the ground floor of a dwelling; the binder used was dark quicklime. In Egypt, there is a description of the use of mortar and concrete [3] on a wall in Thebes dating from 1950 BC.

The use of this type of material definitely spread throughout all of the Mediterranean and was frequently used for Roman buildings, involving mixtures of stone and sand (sometimes pozzolanic in nature) with lime, which were resistant even when exposed to water [4]. Some structures built at the time still stand today, including aqueducts, bridges, quays, breakwaters and large buildings.

One record of the use of concrete in Roman times, which is still in existence today, dates from the beginning of the second century (118–125 AD), when the Pantheon in Rome was rebuilt by the emperor Hadrian, after being destroyed by a fire. Concrete was particularly used to build the dome of this monument (Fig. 4.1), using pumice stone as a coarse aggregate to reduce the weight of the structure. The dome is grandiose, not only because of its size (around 44 m in diameter) and the type of construction but also because of its excellent condition after almost 2,000 years.

Vitruvius' books on architecture [5] written in the first century BC discuss the construction technology and materials used then by the Romans. The same construction processes were used without substantial differences until the nineteenth century, a time when the Industrial Revolution brought technical innovations and

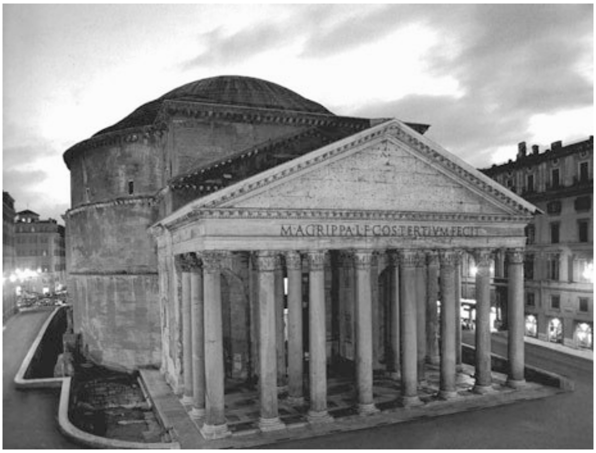


Fig. 4.1 Pantheon in Rome

scientific discoveries that led to the use of concrete as a leading material in construction [4, 6]. Among these innovations, the advent of hydraulic binders was notable, following approval of the patent for the process of obtaining Portland cement (the name given because the colour of the cement was similar to the rock found on the Isle of Portland), produced by Joseph Aspdin in Leeds in 1824.

Although a binder that sets quickly in contact with water had been discovered—hydraulic Portland cement—only with the dawn of reinforced concrete did the use of concrete really revolutionise the construction industry. Like natural rock, concrete has good compressive strength but is fragile when subjected to tensile stress. Therefore, the use of reinforcements—steel bars—provides the reinforced concrete with compressive and tensile strength. A boat made using this technology is believed to have been made by Jean-Louis Lambot in 1848 (Fig. 4.2) and is considered to be the oldest reinforced concrete structure [7].

As well as the development of concrete as a construction material, Feret's study on pastes, published in 1892, was highly important. It presents the fundamental law that relates the material's strength to its compacity: $\sigma_r = c/(a + v)$, where σ_r is strength; c, cement content; a, water content; and v, void content of the mixture. From this fundamental law, it can be inferred that concrete's strength is inversely proportional to the amount of water used in the mixing stage.

Among the first uses in Portugal, special mention should be made of the wheat mill building in Caramujo (Cova da Piedade), built in 1898, where the Sociedade Industrial Aliança mill was later located, and the Vale de Meoes Bridge, nearby Mirandela, which can be seen in Fig. 4.3 in 1904 when it was still under construction [7].

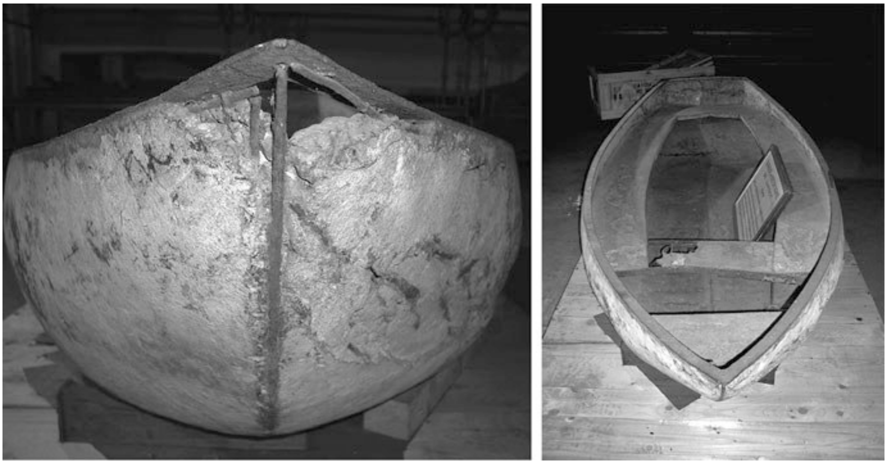


Fig. 4.2 First structure made of reinforced concrete (1848)

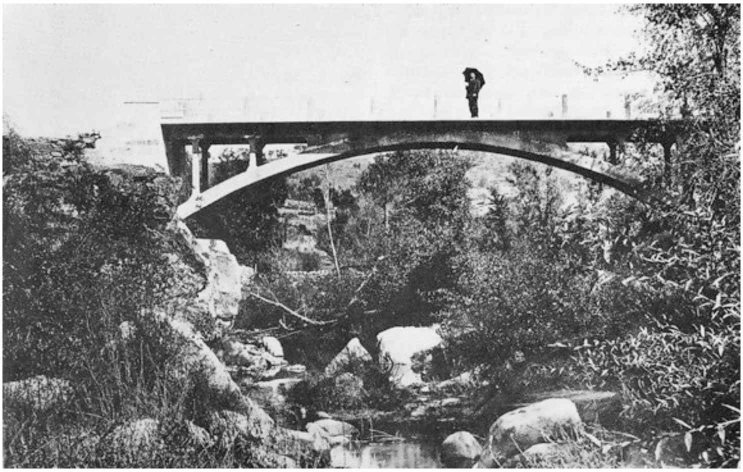


Fig. 4.3 Vale de Meoes Bridge at Mirandela (1904)

4.1.3 Regulatory Framework

The regulations governing concrete were defined by Executive Law No. 301/2007, of 23 August 2007, which establishes the conditions for putting concrete with hydraulic binders on the market and for executing concrete structures. This executive law uses the regulatory references EN 206 “Concrete. Specification, performance, production and conformity” for the specification, production and conformity of concrete and EN 13670 “Execution of concrete structures” for matters relating to the execution of structures, cover casting and curing concrete.

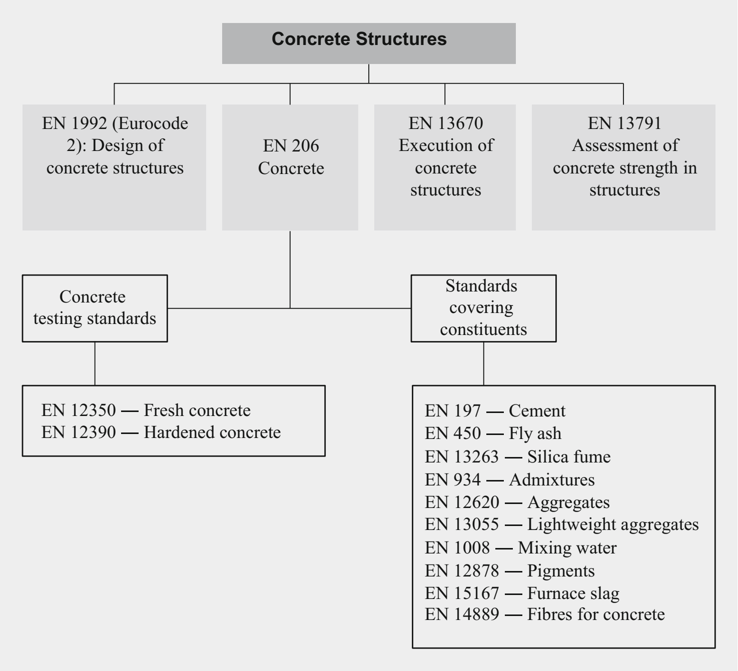


Fig. 4.4 Relationships between EN 206 and standards for designing and execution, standards for constituents and testing standards

Under these terms, it is compulsory to comply with EN 206 and its references to national documents when producing all types of concrete designed for concrete structures made on-site, prefabricated structural products, buildings and civil engineering structures. Concrete may be mixed on site, at a concrete plant or at a precast concrete factory.

This standard, which is part of a range of standards relating to concrete structures (Fig. 4.4), refers to rules for constituents and test methods, depending on the case in question, for concrete and its components. EN 206 specifies requirements for:

- The constituents composing the concrete
- The properties of fresh and hardened concrete and checking those properties
- Limitations to concrete composition
- Specifications for concrete
- Delivering fresh concrete
- Procedures for production control
- Conformity criteria and conformity evaluation

Concrete should be prescribed according to the actions to which it will be exposed. As well as mechanical forces, environmental forces are also considered when establishing the composition of the concrete. Under these terms, EN 206 establishes classes of exposure relating to these environmental actions, organised as shown in Tables 4.1, 4.2, 4.3, 4.4, 4.5, and 4.6.

Table 4.1 Environmental exposure classes without risk of corrosion or attack

Class	Description of environment	Examples
X0	For concrete without reinforcement: all exposure, except freeze/thaw, abrasion or chemical attack	Concrete buried in non-aggressive soil
		Concrete permanently submerged in non-aggressive water
		Concrete with wet/dry cycles not subjected to abrasion, freeze/thaw or chemical attack
	For reinforced concrete: very dry	Reinforced concrete in a very dry environment
		Concrete inside buildings with very low air humidity

Table 4.2 Environmental exposure classes with risk of corrosion induced by carbonation

Class	Description of environment	Examples
XC1	Dry or permanently wet	Reinforced concrete inside buildings or structures, except in areas with high humidity
		Reinforced concrete permanently submerged in non-aggressive water
XC2	Wet, rarely dry	Reinforced concrete buried in non-aggressive soil
		Reinforced concrete subjected to long periods of contact with non-aggressive water
XC3	Moderate humidity	External surfaces of reinforced concrete sheltered from rain
		Reinforced concrete inside structures with moderate or high air humidity (e.g. kitchens, bathrooms)
XC4	Alternately wet and dry	Reinforced concrete exposed to wet/dry cycles
		External surfaces of reinforced concrete exposed to rain or not included in class XC2

Table 4.3 Environmental exposure classes with risk of corrosion induced by chlorides not from sea water

Class	Description of environment	Examples
XD1	Moderate humidity	Reinforced concrete in parts of bridges away from the direct action of de-icing salts but exposed to airborne chlorides
XD2	Wet, rarely dry	Reinforced concrete completely immersed in water containing chlorides; swimming pools
XD3	Alternately wet and dry	Reinforced concrete directly affected by de-icing salts or by splashed by water containing chlorides[a]
		Reinforced concrete in which one of the surfaces is immersed in water containing chlorides and the other is exposed to the air (e.g. some swimming pools or parts thereof). Slabs for car parks[b] and other flooring exposed to salts containing chlorides

[a] In Portugal, these situations should be considered as class XD1
[b] Idem, when relevant

Table 4.4 Environmental exposure classes with risk of corrosion induced by chlorides from sea water

Class	Description of environment	Examples
XS1	Exposed to air carrying sea salts but no direct contact with sea water	Reinforced concrete in a salt-saturated maritime environment
		Reinforced concrete in coastal areas close to the sea, directly exposed and less than 200 m from the sea; this distance may increase to up to 1 km on flat coasts and river estuaries
XS2	Permanently submerged	Permanently submerged reinforced concrete
XS3	Tidal, splash and spray zones	Reinforced concrete subjected to tides or splashing, up to 10 m above the high tide level (5 m on the south coast of mainland Portugal) and up to 1 m below the low tide level Reinforced concrete in which one of the surfaces is immersed in sea water and the other is exposed to the air (e.g. submerged tunnels or tunnels open in rock or soil permeable to the sea or in river estuaries). This type of exposure will very probably require extra protection measures

Table 4.5 Environmental exposure classes with risk of freeze/thaw attack

Class	Description of environment	Examples
XF1	Moderate number of freeze/thaw cycles, without de-icing products	Concrete in vertical surfaces exposed to rain and freezing
		Concrete in non-vertical surfaces exposed to rain and freezing
XF2	Moderate number of freeze/thaw cycles, with de-icing products	Concrete, such as on bridges, which can be classified as XF1 but directly or indirectly exposed to de-icing salts

When concrete is classified according to its compressive strength, Table 4.7 applies for normal density or heavyweight concrete, and Table 4.8 for lightweight concrete. For classification purposes, a characteristic strength after 28 days is obtained using test cylinders measuring 150 mm in diameter by 300 mm in height ($f_{\mathrm{ck,cyl}}$) or from test cubes with 150 mm sides ($f_{\mathrm{ck,cube}}$).

A range of technical specifications were drawn up, whose application is provided for in EN 206 through its National Application Document, in which instruments are established to support the implementation of EN 206 in the Portuguese market. Application of these specifications is therefore compulsory. The specifications cited are LNEC E 461 “Concrete. Methodology to prevent internal expansive reactions”, LNEC E 464 “Concrete. Prescriptive methodology for a design working life of 50 and 100 years under the environmental exposure” and LNEC E 465 “Concrete. Methodology for estimating the concrete performance properties allowing to comply with the design working life of the reinforced or prestressed concrete structures under environmental exposures XC and XS”.

Table 4.6 Limits for exposure classes for chemical attack from natural soils and the water within them

Chemical characteristic	Testing method of reference	Class XA1	Class XA2	Class XA3
Water				
SO_4^{2-}, mg/L	EN 196-2	$\geq$200 and $\leq$600	>600 and $\leq$3,000	>3,000 and $\leq$6,000
pH	ISO 4316	$\geq$5.5 and $\leq$6.5	$\geq$4.5 and <5.5	$\geq$4.0 and <4.5
CO_2 aggressive, mg/L	EN 13577	$\geq$15 and $\leq$40	$\geq$40 and $\leq$100	>100 up to saturation
NH_4^+, mg/L	ISO 7150-1 or ISO 7150-2	$\geq$15 and $\leq$30	$\geq$30 and $\leq$60	$\geq$60 and $\leq$100
Mg^{2+}, mg/L	ISO 7980	$\geq$300 and $\leq$1,000	$\geq$1,000 and $\leq$3,000	>3,000 up to saturation
Soil				
SO_4^{2-}, total mg/kg	EN 196-2	$\geq$2,000 and $\leq$3,000	>3,000 and $\leq$12,000	>12,000 and $\leq$24,000
Acidity, mL/kg	EN 16502	>200 Baumann Gully	Not found in practice	

Table 4.7 Compressive strength classes for normal density concrete and heavyweight concrete

Class	C8/10	C12/15	C16/20	C20/25	C25/30	C30/37	C35/45	C40/50
$f_{ck,cyl}$ (MPa)	8	12	16	20	25	30	35	40
$f_{ck,cube}$ (MPa)	10	15	20	25	30	37	45	50
Class	C45/55	C50/60	C55/67	C60/75	C70/85	C80/95	C90/105	C100/115
$f_{ck,cyl}$ (MPa)	45	50	55	60	70	80	90	100
$f_{ck,cube}$ (MPa)	55	60	67	75	85	95	105	115

Table 4.8 Compressive strength classes for lightweight concrete

Class	LC8/9	LC12/13	LC16/18	LC20/22	LC25/28	LC30/33	LC35/38
$f_{ck,cyl}$ (MPa)	8	12	16	20	25	30	35
$f_{ck,cube}$ (MPa)	9	13	18	22	28	33	38
Class	LC40/44	LC45/50	LC50/55	LC55/60	LC60/66	LC70/77	LC80/88
$f_{ck,cyl}$ (MPa)	40	45	50	55	60	70	80
$f_{ck,cube}$ (MPa)	44	50	55	60	66	77	88

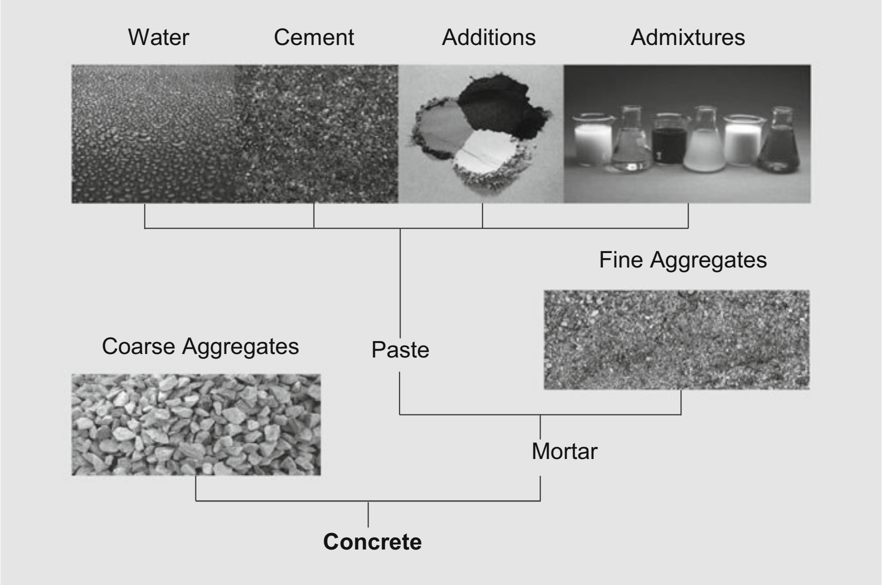


Fig. 4.5 Concrete composition

Specification LNEC E 461 identifies the rocks and minerals that may be potentially reactive to alkalis, defines methodologies for assessing the reactivity of aggregates and the possibility of concrete compositions having internal expansive reactions and establishes measures to avoid expansive reactions occurring through alkali-silica reactions or by delayed ettringite formation.

Specification LNEC E 464 establishes the aptitude of hydraulic binders—cements and mixtures of cements and additions—as concrete constituents, clarifies the selection of exposure classes into which the aggressive environmental actions for concrete are organised in EN 206 and defines the prescriptive measures that allow the 50- or 100-year designed working life for concrete structures to be met, in environments that correspond to the different exposure classes. This specification further establishes the general framework for guaranteeing the designed working life of the concrete structures and the aptitude of the equivalent performance concept.

Specification LNEC E 465 establishes a methodology for estimating the performance properties of reinforced or prestressed concrete subjected to carbon dioxide or chloride action, which allows the working life desired to be met.

4.1.4 Constituents

As mentioned in the introduction, the main constituents of concrete include cement, additions, admixtures, aggregate and water (Fig. 4.5). The range of fine material—

Table 4.9 Proportions of concrete constituents

Constituent	Binder	Aggregates	Water	Air
Volume (%)	7–14	60–78	14–22	1–6
Mass (%)	9–18	63–85	5–9	–

cements and additions—is called binder. The mixture of binder, water and admixtures forms the concrete paste. Introducing fine aggregate, known as sand, leads to the formation of mortar. The use of coarse aggregate is what differentiates concrete from mortar. Normally, concrete is considered a two-phase composite: paste and aggregate. Table 4.9 shows the most common ranges for content, in volume and mass, of the main constituents of concrete [8].

A brief description of the main constituents of concrete will be given in the following sections.

4.1.4.1 Cement

Cement is a mineral powder that sets and hardens even under water, which is why it is known as a hydraulic binder. It forms a paste with water and progressively sets and hardens in the air or in water. The set of reactions that lead to hardening are generally called hydration. Cement is the fundamental constituent of concrete because it allows a non-cohesive mixture to become a solid mass.

Cement is obtained by burning a mixture of limestone and clay, with appropriate proportions, in rotating kilns with small quantities of other minerals, thereby obtaining a composite known as clinker. This composite is then milled and mixed with calcium sulphate (gypsum) and, possibly, with other substances.

The main components of cement are:

- Tricalcium silicate (C3S), forming around 20–80 % of the weight of cement, is the component responsible for the start of the setting process and early strength, since it is the substance that hydrates and hardens most quickly.
- Dicalcium silicate (C2S), in amounts between 10 and 55 %, hydrates and hardens slowly, helping form later strength (beyond 7 days).
- Tricalcium aluminate (C3A), 0–15 %, is the constituent that reacts earliest with water, releasing a great amount of heat in the first stages and slightly helping to develop initial strength. When cement has smaller amounts of tricalcium aluminate, it is more resistant to sulphates.
- Tetracalcium aluminoferrite (C4AF) hydrates quickly but does little to help strength. Its presence in cement varies between 5 and 15 %. Cement's grey colour is due to the presence of iron in this compound.
- Calcium sulphate (CS) is added in amounts up to 5 % after the clinker has been obtained in order to delay the fast setting of the aluminates with the water.

The fundamental compounds formed in cement hydration are calcium silicate hydrates (C-S-H), responsible for the main strength characteristics of hydrated cement, and calcium hydroxides (CH). Smaller quantities of calcium aluminate hydrates (C-A-H) and calcium aluminium sulphates, known as ettringite, are also formed. This last constituent is very important because it is potentially expansive.

The main reactions that occur during contact between water and cement are the following:

- $\mathrm{C3S + Water \rightarrow C\text{-}S\text{-}H + CH}$
- $\mathrm{C2S + Water \rightarrow C\text{-}S\text{-}H + CH}$
- $\mathrm{C3A + CS + Water \rightarrow Ettringite\ (calcium\ aluminate\ trisulphate)}$
- $\mathrm{C4AF + Water \rightarrow C\text{-}(A, F)\text{-}H}$
- $\mathrm{C3A + CH + Water \rightarrow C\text{-}A\text{-}H}$

Figure 4.6 shows the relative content of the different compounds produced by hydration reactions over time. Evolution in the porosity of the mixture is also shown—it reduces with the formation of hydration products, with amounts remaining proportional to the water–cement ratio (W/C). The formation of monosulphoaluminate arises from the conversion of ettringite, due to the lack of sulphate ions in the solution.

The standards that currently regulate cement production are as follows: EN 197-1 "Cement. Part 1: Composition, specifications and conformity criteria for common cements" and EN 197-2 "Cement. Part 2: Conformity evaluation". The test methods are described in the different parts of standard EN 196 "Methods of testing cement".

In accordance with EN 197-1, five main types of cement are established: CEM I, which essentially contains clinker (95–100 %); CEM II, which adds an abbreviation referring to the addition that replaces clinker up to a limit of 6–35 %; CEM III, generally known as blast furnace slag cement, since it consists of a mixture of clinker with 36–95 % ground blast furnace slag; CEM IV, which is the result of a mixture of 11–55 % pozzolanic material, commonly known as pozzolanic cement; and CEM V, composite cement, which is the result of combining slag and pozzolans up to a total content of these additions of 36–80 % of the mass of cement.

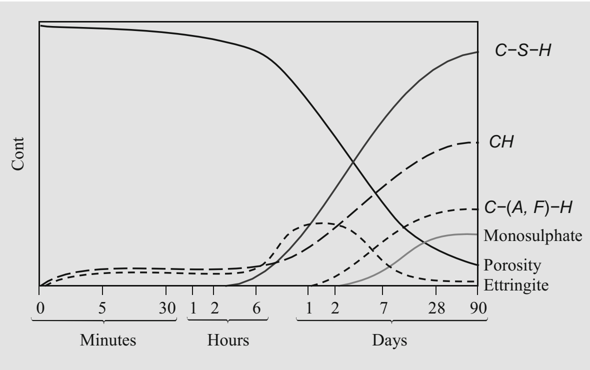


Fig. 4.6 Relative quantities of compounds formed during hydration

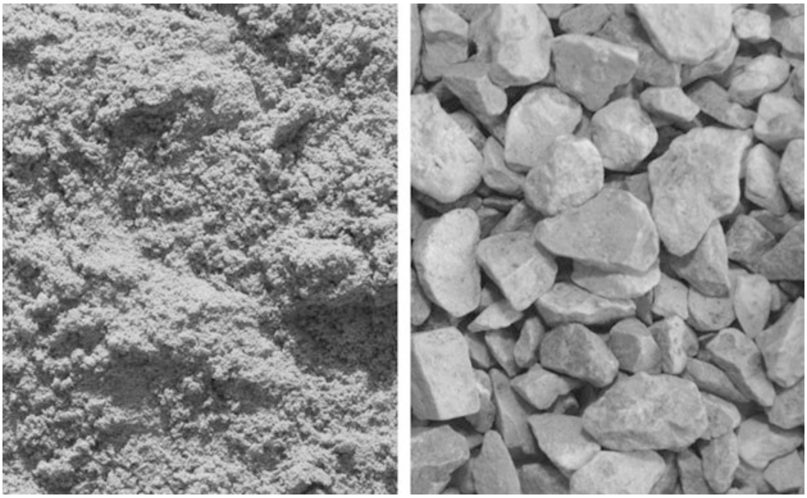


Fig. 4.7 Aggregates of different sizes

Considering those five main types and the many types and content levels of additions allowed, it is possible to produce 27 different types of cement. And bearing in mind the different strength classes, those combinations may reach up to 162 types, without including white cements. In Portugal, 15 cements of three main types are currently produced: CEM I (I 42.5R; I 52.5R; I 52.5R(br)); CEM II, with limestone filler (II/B-L 32.5N; II/A-L 42.5R; II/B-L 42.5R; II/B-L 32.5R(br); II/B-L 52.5N(br)), pozzolans (II/A-P 42.5R; II/B-P 32.5N), or fly ash, and limestone filler with additions (II/B-M(V-L) 32.5N; II/B-M(V-L) 42.5R); and CEM IV, with fly ash (IV/A(V) 32.5R; IV/B(V) 32.5N; IV/B(V) 32.5R) (Fig. 4.7).

4.1.4.2 Aggregates

Aggregate is considered to be all granular material suitable for use in concrete. Aggregates may be natural, artificial, reclaimed or recycled from material previously used in construction.

The main functions of aggregate in concrete can be summarised as follows: acting as a filler, reducing costs, providing strength and durability and reducing changes in volume due to the hydration and drying processes.

Aggregates may be considered as concrete's skeleton, and as they make up most of its volume (Table 4.9), their characteristics condition the quality of the concrete. It could be said that their mineral characteristics affect the physical properties of the concrete in its hardened state, while the geometric characteristics mostly influence concrete's behaviour in its fresh state.

In fact, the influence of aggregates on concrete's behaviour is significant, particularly in its hardened state. Until a few years ago, aggregates were known as inert material. However, these particles are far from inert, since their characteristics condition the concrete's behaviour through a variety of actions.

Their deformability and porosity act in a physical way, conditioning the movements of expansion and shrinkage of the concrete.

Aggregates may also act chemically, affecting the integrity of the concrete if they are reactive to alkalis. On the other hand, there may be reactions between the aggregates and the cement, creating epitaxial bonds. The effects of thermal action may also take place, with the aggregates dilating or contracting, contributing to the deformation of the concrete.

Aggregates may only be used in concrete if the requirements of standard EN 12620 “Aggregates for concrete” are met. In the case of lightweight aggregates, standard EN 13055-1 applies: “Lightweight aggregates—Part 1: Lightweight aggregates for concrete, mortar and grout”. Nonetheless, as these standards do not cover most properties, in terms of demands, the following Portuguese regulatory documents were drawn up:

- LNEC E 467 “Guide to the use of aggregates in hydraulic concrete”
- LNEC E 471 “Guide to the use of coarse recycled aggregates in hydraulic concrete”

The main testing standards referred to in the product standards above are as follows:

- EN 932 “Tests for general properties of aggregates”
- EN 933 “Tests for geometrical properties of aggregates”
- EN 1097 “Tests for mechanical and physical properties of aggregates”
- EN 1744 “Tests for chemical properties of aggregates”
- EN 1367 “Tests for thermal and weathering properties of aggregates”

Aggregates can be classified according to origin, petrography, density and size.

Depending on their origin, they can be classified as natural aggregates, of mineral origin, which have been subjected only to mechanical processing, being crushed or milled. Artificial aggregates, of mineral origin, result from an industrial process involving thermal or other types of modification. Reclaimed aggregates are gained either by washing fresh concrete or by crushing hardened concrete that has not been previously used in construction. Recycled aggregates result from the processing of inorganic materials previously used in construction.

In terms of petrography, aggregates may come from igneous rock, sedimentary rock or metamorphic rock. Classification according to density (ρ) is divided into three classes: heavyweight, $\rho > 2{,}800$ kg/m^3; normal, $2{,}000$ kg/m$^3 > \rho > 2{,}800$ kg/m^3; and lightweight, $\rho < 2{,}000$ kg/m^3. Size distinguishes coarse aggregates, with a maximum particle size (*D*max) higher than 4 mm, and fine aggregates, with a *D*max equal or lower than to 4 mm. Filler aggregates are also identified, with a *D*max of 0.063 mm.

4.1.4.3 Additions

According to EN 206, additions are finely divided inorganic constituents used in concrete in order to improve certain properties or to achieve special properties. They are classified into two types: almost inert additions (type I) and pozzolanic additions or additions with latent hydraulic characteristics (type II).

Type I additions, specifically limestone filler, which is common in Portugal, essentially has the role of increasing the compacity of the paste, reducing porosity and subsequently making it possible to maintain strength with less clinker, thus reducing the cost of binder. Pigments are another type I addition and are added to concrete to give it colour. The use of pigments is more effective if used with white cement, except when black concrete is desired.

The most common type II additions are natural pozzolans, fly ash, silica fume and grinded blast furnace slag. Apart from natural pozzolans, these additions come from industrial waste and by-products, so their use is advantageous for economic and environmental reasons. Apart from blast furnace slag, which has latent hydraulic characteristics, the effectiveness of the additions depends on their pozzolanicity. Pozzolanicity determines the ability of reactive silica in the addition to react with the calcium hydroxide resulting from the hydration of the cement, forming calcium silicate hydrates.

This reaction, known as the pozzolanic reaction, has three effects on concrete: firstly, the reaction is slow and, as such, the heat released and strength growth are slow; secondly, the reaction consumes calcium hydroxide, which is good for durability in acid environments and whenever there may be leaching; thirdly, the porosity is reduced, since the products of the pozzolanic reaction refine the porosity, improving the sealing qualities and strength of the material.

The product standards and specifications that regulate the additions available in the Portuguese market are as follows:

- LNEC E 466 “Limestone fillers for hydraulic binders”
- EN 12878 “Pigments for the colouring of building materials based on cement and/or lime. Specifications and methods of test”
- NP 4220 “Pozzolans for concrete. Definitions, specifications and conformity evaluation”
- EN 450-1 “Fly ash for concrete. Part 1: Definition, specifications and conformity criteria”
- EN 13263-1 “Silica fume for concrete. Part 1: Definitions, requirements and conformity criteria”
- EN 15167-1 “Ground granulated blast furnace slag for use in concrete, mortar and grout. Part 1: Definitions, specifications and conformity criteria”

4.1.4.4 Admixtures

Admixtures are products added in small quantities (no more than 5 % compared with the mass of cement) during the concrete mixing process to modify the properties of fresh or hardened concrete. Admixtures, when they were first used, were formed of industrial waste, but are now developed and produced responding to specific demands of concrete. They are not cheap products, but they lead to some financial savings, by reducing the workforce needed for compacting work, using less cement and increasing the durability of the concrete, for example.

Admixtures for concrete are regulated by EN 934-2 “Admixtures for concrete, mortar and grout. Part 2: Concrete admixtures. Definitions, requirements, conformity, marking and labelling”. Admixtures can be classified into the following groups: rheology modifiers, setting modifiers, air-entraining agents, water repellents and shrinkage controllers.

Among those that modify rheology, that is, the concrete’s deformation and fluidity properties in fresh state, water reducers and viscosity modifiers stand out.

Water reducers, plasticisers and superplasticisers are the most commonly used, since they allow the water content in a given concrete to be reduced without affecting consistency, or they allow the fluidity of a concrete to be increased without increasing water dosage, or both effects at once. Among the water reducers, superplasticisers stand out for their stronger ability to reduce water compared with plasticisers. Water reducers are used in manufacturing practically all concrete, since they allow very fluid fresh concrete to be produced even with low water content, broadening the range of practical possibilities. Pumping concrete and, recently, self-compacting concrete are the result of developments in water reduction technology, particularly superplasticisers. Due to their ability to decrease the W/C ratio while maintaining consistency, water reducers lead to savings in cement, for concrete of the same strength, or increased durability thanks to reduced porosity. Their importance justifies a brief description of the mechanisms behind the efficiency of water reducers.

Cement particles, in a water solution, tend to agglomerate because of their size and their electrical surface charge. Agglomeration affects negatively the fluidity of the mixture. As such, it will be necessary to increase water content, i.e. the W/C ratio, to obtain a more fluid mixture. When water reducers are introduced into the mixture, since they are polymers with parts of their chains charged with the opposite signal to that of the cement particles, they tend to be immediately absorbed into the surface of the cement. The process of particle dispersion generally takes place because of two mechanisms, which can occur simultaneously or not, depending on the type of polymer: electrostatic repulsion and steric repulsion (Fig. 4.8).

Electrostatic repulsion arises from the creation of electric potential (normally negative) by the admixtures on the surface of the cement particle. This generates a difference in potential, known as zeta potential (ζ), between the surface and any point in the system, which stops particles from coming closer together.

Steric repulsion is due to the size and orientation of the side chains of the polymers, which extend throughout the solution, forming a structure that stops neighbouring particles that have been absorbed by the same admixture from coming closer together.

Viscosity-modifying admixtures (VMAs) can be used in concrete production, particularly self-compacting concrete, in order to improve segregation resistance, namely bleeding, increasing the viscosity of the paste. They also allow a wider

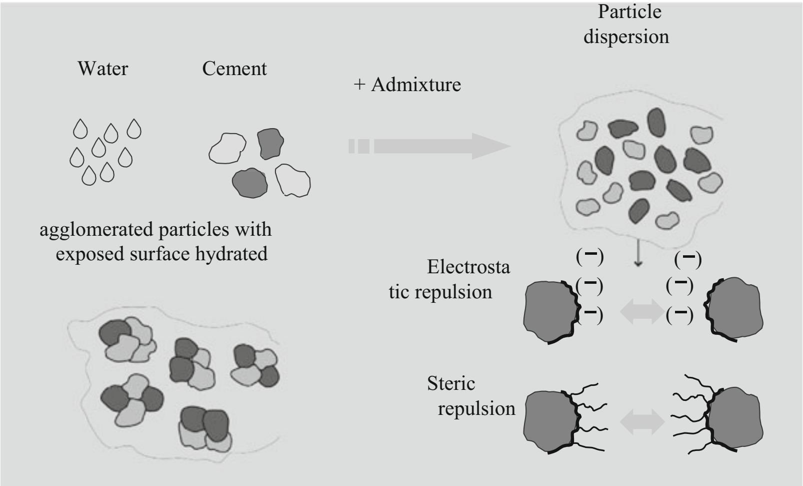


Fig. 4.8 Diagram of the influence and mechanisms for dispersing particles by the admixture

range of materials to be used, such as aggregates with different particle sizes and grinded sand, as well as mitigating the effects of variations in the materials and their proportions in the concrete [9]. VMAs are also known as stabilisers, viscosity improvers or, according to the general definition in standard EN 934-2, water retainers.

Setting modifiers include setting accelerators and retarders, which reduce and increase, respectively, the time it takes for concrete to be transformed from a plastic state to a hardened state, and hardening accelerators, which increase the speed of development of initial concrete strength, with or without a change in setting time.

Air-entraining agents allow a controlled amount of small air bubbles to be incorporated during mixing, which are uniformly spread throughout the mixture and remain after hardening. The use of water repellents aims to reduce capillary action water absorption by the hardened concrete.

Shrinkage controllers, although not considered in EN 934-2, have been used, as their name suggests, to reduce shrinkage of the concrete, acting on the capillary stress of its pores.

4.1.4.5 Water

The amount of water in the concrete composition is very important for the concrete's behaviour, specifically its strength. An increase in water content leads to lower strength.

In fact, cement needs around 23 % of its weight on water in order to fully hydrate. Nonetheless, not all cement is hydrated and higher water contents are used to produce and apply concrete under physically and economically acceptable conditions. Therefore, the remaining water, which can evaporate, will contribute to the formation of a network of pores inside the concrete, affecting not only its strength but also its durability.

The quality of the water to be used in the concrete should also be assessed. Impurities that may be present in the water can interfere with the setting of the cement, affect the concrete's strength, form stains on the surface and, if it contains chlorides, corrode the reinforcements.

If the water is drinking water, it is suitable for concrete production, in accordance with EN 1008 "Mixing water for concrete. Specification for sampling, testing and assessing the suitability of water, including water recovered from processes in the concrete industry, as mixing water for concrete". As regards water from other sources, its suitability should be checked according to the test procedures indicated in EN 1008. Waste water is not suitable for use in cement.

4.1.4.6 Fibres

Fibres are not considered among the basic constituents of concrete and are used in the composition to better control cracking, namely in flooring, by strengthening the tensile characteristics of the concrete matrix, which is considered to be weak.

The fibres can be steel, glass, synthetic (acrylic, carbon, nylon, polyester, polyethylene, polypropylene) or natural (coconut, jute, bamboo, sisal).

Steel fibres are regulated by EN 14889-1 "Fibres for concrete. Part 1: Steel fibres. Definitions, specifications and conformity", and polymer fibres by EN 14889-2 "Fibres for concrete. Part 2: Polymer fibres. Definitions, specifications and conformity". The test methods to characterise them are described in EN 14845 "Test methods for fibres in concrete".

4.1.5 The Diversity of Concrete

4.1.5.1 Diversity of Uses

Since the advent of reinforced concrete, at the end of the nineteenth century, it has been used in the most varied of ways, thanks to its versatility as a construction material. Different types of technology have been developed to give concrete a range of uses that are hard to match with other construction materials.

The versatility of manufacturing, transporting and applying concrete, as well as its competitive cost, means it has been used for many different projects. These uses include foundations, flooring, support walls, buildings, roads, bridges, tunnels, dams, conduits, chimneys, silos, reservoirs, quays and other maritime structures, prefabricated elements such as railways sleepers, beams and other structures. As many structures reach the end of their working life, they need to be strengthened or repaired. Use of concrete in that field has therefore seen an increase in recent years.

4.1.5.2 Diversity of Types of Concretes

Concrete must be adapted to different ways of manufacturing, transporting, casting and compacting and, furthermore, specific behaviour demands.

There are two manufacturing methods: at a concrete plant or on-site. Among the means of transport, there are concrete trucks, with or without mixing accessories; conveyor belts; simple trucks; buckets; and tractors. The means of casting concrete can also be very different, such as concrete cast using a bucket, pumped concrete, sprayed concrete, concrete placed using trucks and tractors and concrete laid using conduits.

The following are situations in terms of concrete compaction: without compaction; by hand with compacting rod or bar; compaction using an immersed vibrator; external compaction using a formwork vibrator; external compaction using a vibrating table; compaction caused by the rate of pouring; external compaction through compression and vibration; vacuum compaction; and screed compaction.

In terms of specific demands, it is more and more common that concrete is prescribed with controlled shrinkage, limited bleeding, low hydration heat, high strength, light weight and high durability, among other characteristics. In light of the many possible uses of concrete, several types of concrete were developed, based on the specific characteristics of the application process.

Among the types of concrete whose names are related to their most important characteristic, we find white/coloured concrete, polymer concrete [10], self-compacting concrete [11, 12], reactive powder concrete, high-performance concrete [13], lightweight concrete [14], concrete with fibres and controlled shrinkage concrete. Among the concrete named for its function, we find filler concrete, underwater concrete [15], mass concrete, precast concrete [16], shotcrete [17] and roller-compacted concrete [18].

4.2 Properties of Concrete

The characterisation of concrete should be made depending on its state: fresh or hardened. In fresh state, all its properties that allow production, transport, handling, pouring and compaction are taken into consideration. After it has compacted and its surfaces have been finished, concrete enters its hardened state and it begins to undergo different structural and environmental actions.

4.2.1 Behaviour in Fresh State

The period when the concrete is in its fresh state is insignificant in comparison to its total lifetime. Nonetheless, many operations are carried out during this short time, such as mixing, transporting, pouring, compacting and finishing. These operations are dependent on concrete's behaviour during its fresh state and influence the quality of the structure, since they affect its degree of compaction, strength, homogeneity, the appearance of its surfaces, waterproofing, etc.

Concrete's behaviour in its fresh state is assessed, essentially, by its workability, although in recent years the concept of rheology has been used, specifically in the development and use of fluid concrete. Other properties allow the conformity and stability of the concrete to be assessed when in this state. They include density, air content, setting time and resistance to segregation.

4.2.1.1 Concept of Workability

Workability is an idea associated with a greater or lesser ease with which a certain concrete is transported, poured, compacted and finished, while maintaining its homogeneity throughout these operations. It is not a property intrinsic to concrete, since it also takes into consideration local conditions and the means used to transport, pour, compact and finish the concrete. As an example, a dry concrete that has good workability to execute roller-compacted concrete dams would have poor workability for producing thinner elements such as columns and beams for buildings. Characterising workability should therefore take into account the specific conditions of the concrete structure to be made.

EN 206 uses the concept of consistency to characterise workability. This concept is related to the material's capacity to keep its form, after being moulded, or, conversely, how difficult it is for the material to flow.

4.2.1.2 Test Methods

Checking consistency is fundamental during concrete operations, since it makes it possible to detect alterations in the composition and constituents. For example, an increase in fluidity may indicate a higher moisture content in the aggregates, that the concrete has more water or even that there have been changes in the aggregate particle size.

The test methods for checking consistency, described as follows, are established in EN 206: slump, compactibility and flow table. Test methods to consider self-compacting concrete are also referred in EN 206: slump flow, V-funnel flow, L-box, segregation resistance and J-ring

The most common method for characterising concrete consistency is the slump test, not only because it is easy to perform but also because it is appropriate for most concrete. The procedure for this method is described in EN 12350-2 "Fresh concrete tests. Part 2: Slump test" and requires a cone-shaped mould measuring 20 cm in diameter at the base, 10 cm at the top and 30 cm in height. This mould is known as an Abrams cone, and there is not a work site in the world that does not have one of these cones. During the test, the cone is lifted vertically, after being filled with concrete and duly compacted. The difference between the height of the mould and the height of the centre of the upper edge of the possibly deformed cone of concrete is measured (Fig. 4.9).

In Table 4.10, some examples of uses are given, depending on the concrete slump. These limits are not strict and are guide values only.

For very cohesive concrete, the method provided is the Vebe vibration and compaction test, or simply the Vebe test. This method is described in EN 12350-3 "Testing fresh concrete. Part 3: Vebe test". Fresh concrete is compacted in a slump mould placed on a vibrating table. The mould is removed vertically and a transparent disc is placed on top of the concrete and carefully lowered until it comes into contact with the concrete. The concrete slump is recorded. The vibrating table is switched on

Fig. 4.9 Slump test

Table 4.10 Uses of concrete depending on slump

Slump (mm)	Use
0–25	Flooring
	Inclined concrete
25–50	Mass concrete
	Flooring
	Foundations
50–150	Horizontal slabs
	Normally reinforced concrete
150–250	Densely reinforced concrete
	Pumped concrete
>250	High-performance concrete
	Self-compacting concrete

and the time (Vebe time) needed for the transparent disc to be fully in contact with the cement paste is measured.

The test for evaluating the degree of compactibility is described in EN 12350-4 “Testing fresh concrete. Part 4: Degree of compactibility”. In this test, fresh concrete is carefully placed in a receptacle, avoiding any compaction. When the receptacle is full, the upper surface is struck off, to the level of the edge of the upper part of the receptacle. The concrete is compacted using vibration, and the degree of compactibility is measured by the distance between the surface of the compacted concrete and the upper edge of the receptacle.

The flow table method determines the consistency of fresh concrete by measuring the flow of concrete across a flat table that is lifted and dropped several times. This method is described in EN 12350-5 “Testing fresh concrete. Part 5: Flow table test”.

The criteria for classifying consistency according to different uses are established in EN 206. For the most used test, five slump classes are indicated in Table 4.11.

Table 4.11 Slump classes

Class	Slump (mm)
S1	10–40
S2	50–90
S3	100–150
S4	160–210
S5	≥220

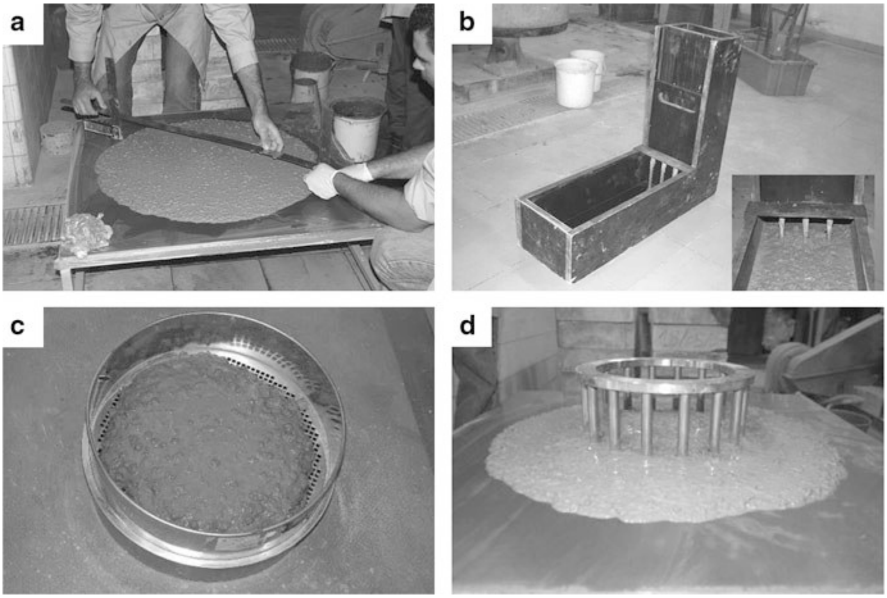


Fig. 4.10 Tests for SCC: (**a**) flow, (**b**) L-box, (**c**) segregation, (**d**) J-ring

Developments in the use of self-compacting concrete (SCC) led to the need to establish standardised procedures for control. The test methods for checking consistency of this type of concrete were therefore regulated. SCC is characterised by its ability to flow and compact under its own weight, filling moulds with the respective reinforcements, sheaths, negatives, etc., while retaining its homogeneous nature. As such, the characteristics to be evaluated are ability to flow (to fill), ability to pass through narrow openings and segregation resistance.

The most commonly used method for checking consistency is slump flow, which is described in standard EN 12350-8 “Testing fresh concrete. Part 8: Self-compacting concrete. Slump-flow test”.

This method is very different from the flow table test (EN 12350-5). In the slump-flow test, the concrete is poured into an Abrams cone without compaction. As soon as the cone begins to be lifted, the time is measured until the concrete spreads out to 500 mm in diameter. This is the t_{500} time. After the concrete has stopped moving, the largest diameter of the spread concrete and the orthogonal diameter are measured (Fig. 4.10a). The spread value corresponds to the average of the two diameters.

The spread and t_{500} time are used to evaluate the fluidity and speed of the SCC flow without obstacles. The spread represents the SCC's ability to fill the space, while the t_{500} time is a measure of the speed of the flow and an indication of the concrete's viscosity.

The viscosity and ability for the SCC to fill space can also be evaluated using the V-funnel test. This test is described in standard EN 12350-9 "Testing fresh concrete. Part 9: Self-compacting concrete. V-funnel test". In this test, a V-shaped funnel is filled and the time taken for the concrete to flow through the lower opening is measured. The value recorded is the V-funnel flow time.

The L-box test (Fig. 4.10b) is used to evaluate the SCC's ability to pass through narrow spaces, such as the space between bars and other obstacles, without segregation or blocking occurring. The test method is regulated by standard EN 12350-10 "Testing fresh concrete. Part 10: Self-compacting concrete. L-box test". In this test, a concrete column is allowed to flow horizontally through a lower opening, through spaces divided by vertical bars. After the flow is complete, the height of the concrete at the furthest point of the box is measured, along with the concrete immediately before the bars. The quotient between the results characterises the passing ability or blocking behaviour of the concrete.

European Standard EN 12350-11 "Testing fresh concrete. Part 11: Self-compacting concrete. Sieve segregation test" describes the test procedure for evaluating SCC's segregation resistance. After the sample has been collected, fresh concrete is left to rest for 15 min, and at the end any sign of water bleeding is recorded. Afterwards, part of the top of the sample is poured through a sieve with a mesh formed of 5 mm openings. After 2 min, the amount of material that has passed through the sieve is measured (Fig. 4.10c). Resistance to segregation is characterised by the amount of material that has passed through and the amount of material poured into the sieve.

The last regulatory test to characterise SCC in its fresh state is the J-ring test (EN 12350-12 "Testing fresh concrete. Part 12: Self-compacting concrete. J-ring test"). Like the L-box test, this test is also used to evaluate the SCC's ability to pass through narrow spaces, such as the space between bars and other obstacles, without segregation or blocking. Nonetheless, these two tests are not directly comparable.

The method follows the procedure described for the slump-flow test (EN 12350-8) with the difference that before the cone is filled, a J-ring is placed on the base, concentrically to the Abrams cone. The J-ring consists of a ring of equally spaced vertical bars (Fig. 4.10d). The difference in height of the concrete between the centre and immediately outside the bars is measured.

4.2.1.3 Factors That Affect Workability

Concrete's workability is influenced by different factors inherent not only to its composition but to the conditions where the concreting takes place. A brief description of some of the most important factors that influence workability will be described, considering workability as the concrete's ease of flow.

The most important of all the factors is water content. The higher it is, the easier the concrete is to handle. This is due to water being the most fluid constituent and because it increases the distance between particles, which makes it easier for the mixture to move.

The type and form of aggregate condition workability, since the rounder it is, the less need there is of paste to move around within the concrete and the lower the energy spent by contact between particles. This is analogous with bearing balls, where sphericity allows movement to occur with less energy.

A wide particle size distribution leads to better workability—smaller particles produce a lubricating effect on the whole.

Another factor that affects workability is the aggregate-paste relationship, since a greater amount of paste makes for more fluidity, because paste can be considered to be the liquid phase of the mixture. The use of water-reducing admixtures has a large influence on workability, since it increases the free water content in the concrete.

The fineness of the cement is proportional to the speed of the loss of workability. The finer the cement, the faster the hydration reactions are.

Environmental conditions also have an influence, namely temperature. Higher temperatures lead to a rapid loss of workability due to increasing hydration rate and evaporation.

4.2.1.4 Rheology

Development in the chemical industry at the beginning of the twentieth century, with the advent of the large-scale production of polymer materials, led to materials with uncommon deformation characteristics. In 1920, studies on these types of materials led to a professor at Lehigh University, Eugene Bingham, to introduce a new term: rheology. The root of this term is from the Greek ρειν, which could be translated as flow [19]. Rheology can be defined as the science that studies the deformation and flow of matter, describing the relationships between force, deformation and time [20, 21].

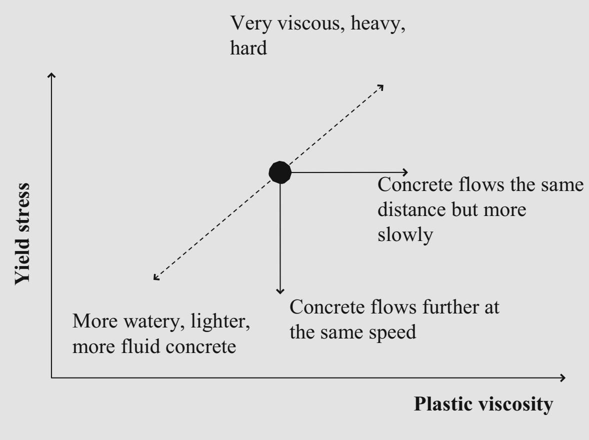
The methods currently used to evaluate workability seek to characterise concrete’s behaviour in its fresh state using a single parameter. It is possible, however, that two concretes can reach the same spread but at different speeds. The deformability of the concrete should therefore be checked, and it depends on at least two parameters. Considering concrete as a Bingham material, in rheological terms, the parameters to be considered are yield stress and plastic viscosity. In this case, and in theory, yield stress is the minimum stress needed for flow to begin, and plastic viscosity corresponds to the variation in stress at a unit of shear rate.

From a practical perspective, yield stress is linked to the concrete’s ability to flow under action from a certain applied stress, expressed by slump or flow. Viscosity is linked to the speed at which concrete flows, once flow has begun.

Although it is important to know the viscosity of concrete for some issues relating to its use, such as pumping and concreting speed, yield stress is the most important parameter for the movement of fresh concrete, namely to fill the formwork.

Considering the process of filling formwork, if the material poured is a purely viscous fluid (with zero yield stress, such as oil), it will self-level due to gravity.

Fig. 4.11 Influence of varying SCC's rheological parameters from the point of view of the person applying the concrete



Gravity introduces a pressure gradient, if the surface of the material is not horizontal. This pressure gradient generates shear stress in the material, which forces it to move until the surface is horizontal and the pressure gradient disappears. In the case of a fluid with yield stress, such as concrete, if the shear stress becomes lower than the concrete yield strength, movement will be interrupted before the concrete self-levels or even before the formwork is completely filled [22]. This description shows that studying the rheological behaviour of concrete is extremely important for the construction industry.

Let us take two different concretes, with the same slump, one with low viscosity and one with high viscosity. The former is easier to handle, while the latter is more viscous and flows more slowly. Fig. 4.11 shows how the effects of altering the rheological parameters of a leading self-compacting concrete (SCC), shown by the dark circle, are experienced by the person applying it.

To characterise rheology, rheometry is used. Rheometry is defined as the range of techniques for performing rheological measurements. There are several processes for measuring the fundamental rheology of fluids. Rheometers are used to take those measurements. A rheometer is an equipment that simultaneously quantifies the deformation and stress histories of a certain material [19].

4.2.1.5 Other Properties in Fresh State

There are other properties of concrete in its fresh state, other than those related to deformability. Among those regulated, whose testing is covered by EN 206, one finds density and air content.

Checking setting times and the tendency towards segregation is also important for characterising the concrete in its fresh state.

Ways of ascertaining density are described in EN 12350-6 "Testing fresh concrete. Part 6: Density". Measuring density is essential for controlling concrete with lightweight or heavyweight aggregates. It is also used to check if the concrete constituents are in the required proportions, compared the overall result with theoretical density. The procedures for checking density involve compacting fresh concrete into a rigid, sealed receptacle, with a known volume, which is then weighed. The quotient between the concrete weight and the receptacle volume is the density.

To evaluate the air content in the concrete, whether air-entraining agents are used or not, the procedure is described in EN 12350-7 “Testing fresh concrete. Part 7: Air content. Pressure methods”. It should be noted that high air content in concrete may lead to lower strength, although it is useful for dealing with freeze/thaw action.

Depending on its composition, concrete may start to set within a few minutes or a few hours. Setting refers to the change from liquid state to solid state, that is, the cement paste becoming rigid. Knowing the time when setting begins is extremely important for concreting operations, as it establishes the period after mixing during which, in theory, the concrete still has adequate workability, and can be transported, handled, laid and compacted without affecting its properties. Setting time may be determined in the binder paste and in the concrete, although it is more usual to do so in the paste, since it is more practical.

The procedures governing the checking of setting time for pastes are described in standard EN 196-3 “Methods of testing cement. Part 3: Determination of setting times and soundness”. For concrete, it is common to adopt the North American procedure ASTM C403 “Standard method of test for time of setting of concrete mixtures by penetration resistance”. Setting time depends on the type of binder, decreasing as the temperature to which the concrete is exposed increases.

Segregation may be defined as the separation of the concrete constituents due to different sizes and densities, so that the concrete is no longer considered to be homogeneous. This phenomenon can be seen in structures where there is an agglomeration of coarse aggregate in the lower part of the elements.

This anomaly may arise for a variety of reasons: inadequate workability, that is, very dry or very fluid concrete, which leads to disaggregation or separation of the constituents, respectively; an excessive amount of coarse aggregate, which increases the difference in densities between solid and liquid phases (the paste); lack of fine aggregate, which reduces the viscosity of the paste; and inadequate laying and compaction, such as concrete falling from a great height or excess vibration.

One particular case of segregation is bleeding. This is due to the rise of water up to the top surface of the concrete. When this occurs in excess, the cement particles and water tend to rise to the surface, reducing the quantity of the paste available to bind to the aggregates. Surface porosity also increases, leading to a dusty surface. It may lead also to a poor binding between successive layers of concrete. Nonetheless, a lack of bleeding may also be a problem, especially for flooring, since the lack of a film of water on the surface leads to the surface of the concrete drying quickly, and it may crack if not properly cured.

4.2.2 Properties in Hardened State

After setting, the concrete begins to harden. In this state, the concrete no longer has plastic behaviour and instead has essentially elastic characteristics. As a result of the continuous nature of the hydration reaction, while there is water and non-hydrated cement available, its characteristics continue to change, stabilising over time. Particularly if it is not subjected to degradation phenomena, concrete keeps getting stronger. Comparisons between characteristics or different concretes should be made under similar test conditions and for the same age.

4.2.2.1 Mechanical Strength Properties

Concrete's strength, particularly its compressive strength, is considered to be its most important property, although other properties relating to deformability and durability cannot be overlooked. Nevertheless, strength provides a general idea of the quality of the concrete, since it is related to the structure of the hydrated binder. Also, concrete's strength is a fundamental parameter for structural calculations, and it is also specified for checking the concrete's conformity.

In practice, concrete's strength, with the same type of constituents and for a specific age and cure in water, fundamentally depends on two factors: the W/C ratio (Fig. 4.12) and the degree of compaction. Both factors affect concrete's porous structure. A high water content is not fully used in the cement hydration reactions, and the remaining water present in the paste creates a porous structure. Deficient compaction does not allow air bubbles to be expelled, making the paste and its bonding with the aggregates more fragile.

The material's resistance to a specific physical action is limited by its limiting strength to rupture or excessive deformation. Rupture in the material may be explained by the mechanics of the rupture, which refers to formation conditions and the propagation of cracks in a material. Concrete has cracks and other discontinuities even if it is not subjected to other external demands, because of many factors, such as shrinkage, bleeding, different variations in the volume of the

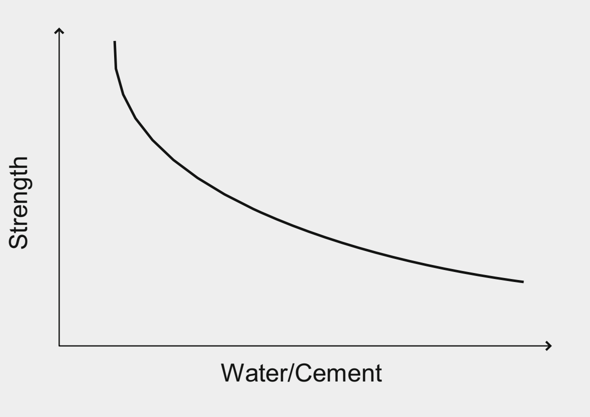


Fig. 4.12 Strength depending on water–cement ratio

cement and aggregate paste, etc. When concrete is put under load from an action, which causes an increase in stress, these cracks are propagated due to the phenomenon of stress concentration, as explained by Griffith's theory.

Concrete resists the actions to which it is subjected in a structure because of several properties. Strength properties include compressive, tensile, shear and flexural strength, which is no more than a combined form of compression and tensile stress.

Compressive Strength

Of these properties, compressive strength is the one evaluated most often and which is used to prescribe concrete. It is used to characterise concrete and to check its constancy and conformity. The standardised method for determining compressive strength is regulated in EN 12390-3 "Testing hardened concrete. Part 3: Compressive strength of test specimens". In this test, specimens are tested up to their rupture in a single-axis compression machine, recording the maximum load supported by the specimen. This value, divided by the cross-sectional area, is used to calculate the compressive strength.

The stress that leads to a rupture in a specimen subjected to a simple compressive force depends on many factors: some relate to the material, such as the W/C ratio, moisture content, aggregate strength, compaction, the type of binder, the cure conditions or age; others depend on test conditions, such as the form and size of the test specimen, the rate of the load and other characteristics of the press.

The W/C ratio conditions the formation of the porous structure. These voids are the weakest parts of the concrete and favour the spread of cracks. The higher the W/C ratio, therefore, the lower the compressive strength. On the other hand, concretes with a higher W/C ratio harden more slowly because the cement particles are closer together and form the structure that provides strength more slowly.

The moisture conditions of the concrete at the time of testing also influence its strength: testing a drier concrete leads to greater strength.

Concrete's strength is influenced by the aggregates, in that the volume that they occupy conditions concrete's behaviour. A poorly compacted concrete has a larger number of voids inside it, which reduces its strength.

Among the cement components, tricalcium silicate and dicalcium silicate are particularly important. The development of cement paste strength until it is 1 year old depends primarily on the proportions of these two components. Cement with high tricalcium silicate content and low dicalcium silicate content will be stronger at an early age, but later growth in strength will be less. On the other hand, cement with a high dicalcium silicate content will have a smaller increase in strength when it is younger, but the growth rate will remain high later on.

The fineness of the cement will also influence the growth of strength, since finer cement represents a larger particle surface to be hydrated, accelerating the respective reactions.

Additions also play a fundamental role in the development of strength in concrete. Pozzolans, such as fly ash, have reaction rates at ambient temperature that are slow, with calcium hydroxide produced by the cement hydration reactions.

Also the reaction of slag is slower than that of the cement. Silica fume, on the other hand, can increase strength at younger ages due to the high fineness of its particles.

Curing conditions, specifically temperature, also condition the speed of the chemical hydration reactions responsible for hardening. The humidity at which the concrete is stored influences strength, since it needs the presence of water for cement hydration to take place. In very dry environments, the surface of the concrete may become excessively dry, and development of the hydration process may be considerably less.

Due to the variation in size of the concrete aggregate and test conditions, the form and size of the test specimens may influence the results of the compressive strength test. Among the causes indicated we find the wall effect, the relationship between specimen size and the maximum aggregate size, internal stress caused by thermohygrometric differences between the surface and the inside and tangential stress due to contact friction between the face of the test specimen and the pressing plate.

Tensile Strength

Although in current calculations it is considered that concrete does not have resistance against tensile stress, knowledge of this property makes it possible to estimate the load under which cracking may occur, due to shrinkage or temperature variation. This property is very important for structures made of mass concrete, such as dams. Other structures, such as roads, may also be calculated depending on their flexural strength, which involves tensile strength.

There are three test methods for tensile strength: direct tensile strength test, direct flexural strength test and diametric compression test. It should be noted, however, that performing the direct tensile strength test free from eccentricity effects is very difficult. Therefore, the other two are the most commonly used methods and have standardised procedures established in EN 12390-5 “Testing hardened concrete. Part 5: Flexural strength of test specimens” and EN 12390-6 “Testing hardened concrete. Part 6: Tensile splitting strength of test specimens”.

Ultimate tensile strength is also influenced by parameters that interfere with compressive strength. However, the interface between the cement paste and the surface of the aggregate is especially important to tensile strength. Concretes with rounded aggregates are, in general, not as strong than those with crushed aggregates.

Shear Strength

Shear behaviour corresponds to the stress necessary for two neighbouring sections to slide along the plane. In pure shear, there is no compressive or tensile stress linked to sliding. For concrete, rupture arising from pure shear is extremely difficult to simulate in a test because the equipment also introduces compressive and tensile stress. Rupture in most cases is due to tensile stress linked to shear forces and not caused by sliding surfaces. The stress necessary to cause breaking in test specimens under shear forces is normally determined, and this information is used when designing the cross section of the structural elements.

The existing test methods introduce compressive and tensile stresses that normally condition the way in which the test specimen ruptures and condition shear strength. For this reason, only results gained from the same method and using specimens that are the same size are comparable.

4.2.2.2 Deformability

Although it is rigid, concrete is a porous material with heterogeneous elements. Knowledge about its deformability properties is important because, just as applying a load is linked to deformation in the concrete, when concrete is deformed without external loads, stresses are introduced. Deformation in concrete while in use—shrinkage, creep and relaxation—is linked to its elasticity.

Modulus of Elasticity

During a load test, at a constant rate, if any deformation is found in the concrete, it can be shown on stress–strain graphs. Stress (σ), as mentioned for strength, represents the quotient of the load (force) applied by the specimen cross section; strain (ε) is the same as the deformation that the specimen undergoes when under the load, to be divided by its initial size.

The stress–strain diagram for the concrete can be split into four phases, depending on the percentage of ultimate strength, which represents different types of behaviour (Fig. 4.13).

In the first phase, with stress lower than around 30 % of ultimate strength, microcracking remains stable and the stress–strain curve is practically linear. In the second phase, above 30 % of the ultimate strength, the increase in stress causes new microcracks to appear in the transition zone and the length and width of existing cracks in this zone to increase. Therefore, part of the deformation is not recoverable and non-linearity begins to be seen, but cracking in the mortar is still incipient up to 50 % of ultimate strength. Above 50 % ultimate strength, in the third phase, cracks in the mortar matrix begin to form, and the cracks in the transition zone take on a considerable size. In the final phase, above 75–80 % ultimate strength, the crack system begins to become unstable and may develop even without increased load. In fact, at this level of stress, the cracks may form in such a way that, even under a constant load, the specimen may break. Above 75 % of ultimate strength, increases in stress make the crack system continuous, due to its rapid growth, both in the mortar and in the transition zone, causing the specimen to break.

The modulus of elasticity or Young modulus, E, represents the stress σ that must be applied to the concrete to achieve unitary deformation, ε. In other words, $E = \sigma/\varepsilon$.

As concrete's behaviour is not entirely linear, the modulus of elasticity represents only the gradient of the right angle formed by joining two points in concrete's stress–strain curve.

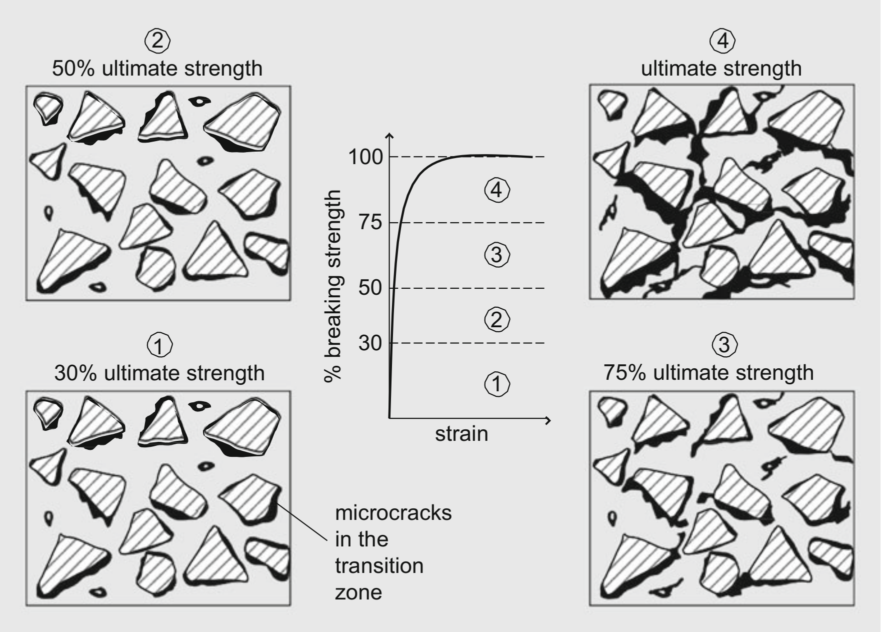


Fig. 4.13 Diagram showing the stress–strain graph for concrete subjected to uniaxial compressive stress

The modulus of elasticity has a different name when calculated using different areas of the stress–strain curve. The modulus of elasticity that is most used in calculations for structures is the secant modulus of elasticity, which is determined based on the strain caused by stress between 0.5 MPa and around 1/3 of the ultimate strength, and the tangent modulus of elasticity, which corresponds to the gradient of the stress–strain curve. The tangent modulus of elasticity is used to calculate effort and deformation due to fast demands, such as seismic actions, and as an estimate of the dynamic modulus of elasticity. Determining the dynamic modulus of elasticity is done with greater precision using sonic tests.

To determine deformation in structures caused by static loads, the secant modulus of elasticity is used. This modulus of elasticity mainly depends on the strength and density of the concrete and also the type of aggregates used. In current concrete, it can range between 25 and 35 GPa.

Poisson's Ratio

The Poisson's ratio of a material is given by the relationship between transversal strain and axial strain under simple axial stress, in elastic phase. The Poisson's ratio for conventional concrete normally ranges between 0.15 and 0.20. In some cases it may reach 0.11 or 0.27. Normally, there is a tendency towards lower ratios in high-strength concretes and higher ratios in saturated concrete and for dynamic actions.

For simple axial stress, when the concrete enters a phase of nonelastic behaviour, lateral deformation grows rapidly, but, in fact, in this case it is not a variation in the material's elastic characteristics but rather deformation due to cracking in the concrete.

Shrinkage

When a material is deformed, in the absence of external forces, and its final size is greater than its initial size, there has been expansion. If its size is smaller than initial size, shrinkage has occurred. In concrete, except for small elements that are submerged in water or containing expansive constituents, there are always shrinkage events. Shrinkage is normally expressed in terms of shrinkage strain, that is, deformation variation compared with initial size.

Generally, concrete shrinks in one of four ways: autogenous shrinkage, drying shrinkage, carbonation shrinkage and shrinkage caused by temperature change.

Autogenous shrinkage occurs in elements that do not have moisture exchange with the outside and is mainly due to hydration reactions. Cement hydration causes the concrete to shrink because it consumes water, and the absolute volume of the hydrated constituents of cement is lower than the sum of the anhydrous constituents and the water with which they react.

Drying shrinkage is due to water leaving the inside of concrete through evaporation. This shrinkage is due to stress in the capillaries and can reach very high levels when external environments are very dry. When drying takes place before the concrete has begun to harden, it is known as plastic shrinkage. Drying shrinkage, during any phase, depends on the following factors: wetness of the concrete, ambient humidity and temperature, wind speed, exposed area/concrete volume ratio (the shape and volume of the specimen), water and cement content in the concrete and curing.

The combination of the carbon dioxide and the products formed from the hydration of cement, mostly calcium hydroxide, also produces solid products with a volume lower than the sum of the volumes of the hydrated components and the volume of the carbon dioxide. This variation in volume is called carbonation shrinkage. It should be noted that this shrinkage is generally small, specifically because it affects a small area of the cross section of structural elements.

Shrinkage caused by temperature change is linked to heat released by the hydration reactions and later cooling.

Creep

The increase in deformation over time of concrete subjected to constant stress is known as creep. The causes of creep are very complicated and can be partially attributed to the movement of water within the concrete and microcracking. Water migration and increased microcracking also contribute to increased deformation. The retarded elastic response of the aggregate is another cause of creep. As the aggregates and the paste are bound, the gradual passing of stress from the paste to the aggregates increases the elastic deformation of the aggregates, contributing to creep.

Generally, creep depends on humidity, ambient temperature, water and cement content, the type of cement and the type of aggregate.

Relaxation

Reduction of stress in concrete subjected to constant deformation over time is known as relaxation; the phenomenon is the opposite of creep, but is dependent on the same phenomena.

Thermal Expansion

All materials dilate with heat. Concrete dilation depends essentially on its composition and the type of aggregates used in particular because of the volume that they occupy. The thermal expansion coefficient varies from $0.7 \times 10^{-5}/°C$, for concrete made using limestone aggregates, to $1.2 \times 10^{-5}/°C$ for concrete made with siliceous aggregates.

4.2.2.3 Density

Concrete density is established by the quotient between the mass of a certain quantity and the volume it occupies. In accordance with EN 12390-7 "Testing hardened concrete. Density of hardened concrete", it can be determined using dry or saturated specimens. The density of concrete depends mostly on the following factors: density of the aggregates; volume of the paste, W/C ratio; and degree of compaction of the concrete. For concrete using regular aggregates, dry density is in the order of 2,400 kg/m^3; with lightweight aggregates, it is less than 2,000 kg/m^3; and with heavyweight aggregates, it produces results of more than 2,600 kg/m^3.

4.2.3 Durability of Concrete

Durability can be defined as the ability of a building, system, component, structure or product to maintain a minimum performance limit for a certain amount of time (working life) under action from degrading factors. According to EN 206, the concept of working life is defined by the period of time for which the performance of the concrete in the structure remains at a level compatible with meeting the structure's performance demands, provided that it is properly preserved.

Concrete in structures is subjected to aggressive agents when it comes into contact with water containing chlorides, sulphates, low pH, aggressive CO_2, ammonium or magnesium, or with soil, due to sulphates and acidity, or with the air, because of the presence of CO_2 and other gases.

The main factors that condition the durability of concrete structures are the dosage and type of cement, W/C ratio, the cover of the reinforcements, laying and curing.

4.2.3.1 Degradation Mechanisms

Concrete, in spite of its qualities, is not eternal and is subjected to several degradation mechanisms. There are two groups of degradation:

Fig. 4.14 Concrete degradation due to corrosion of reinforcements

- Degradation due to corrosion of the reinforcements, either by carbonation of the concrete or the presence of chlorides
- Degradation due to deterioration of the concrete itself, because of internal expansive reactions, shrinkage, chemical attack, biological attack or physical action

Degradation Due to Corrosion of the Reinforcements

The reinforcement inside the concrete are protected from corrosion while they remain passive. When, around the reinforcement, the pH of the concrete decreases or chloride content is high, the steel bars are no longer passive. The products arising from corrosion of the reinforcement inside the concrete tend to occupy a greater volume than the reinforcement. As they are confined inside the concrete, stress is generated in the concrete that may lead to cracking and spalling (Fig. 4.14).

Corrosion of the reinforcements may be caused by carbonation of the concrete. Carbonation is the reaction between carbon dioxide found in the atmosphere and calcium hydroxide found in concrete. The reaction decreases the pH of the concrete surrounding the reinforcements to amounts low enough to stop the reinforcements being passive, making it possible for the corrosion process to begin. The ways of dealing with carbonation involve treating the surface of the concrete, by applying protection so that CO_2 cannot enter the concrete and composing the concrete to mitigate progression of the carbonation front, using binders with high clinker content (CEM I or CEM II) so that the concrete has a high calcium hydroxide (CH) content, which keeps pH levels higher. It should be noted that pozzolanic additions react with CH, reducing its content in the concrete, so using these additions or cements with these additions reduces the concrete's resistance against carbonation.

Another mechanism that leads to corrosion of the reinforcements is the presence of a high level of chlorides close to the reinforcements, which stops them from being passive. The formation of iron oxides is normally spotted at the start and forms a concentration that helps to allow the corrosion process to continue. Chlorides may come from concrete constituents or the external environment (e.g. maritime areas). Resistance to this degradation mechanism involves limiting the chloride content of the concrete constituents and increasing concrete's resistance to diffusion of the chlorides within it. The limits for chloride content are specified in EN 206. Resistance to the diffusion of chlorides is improved in concrete with very low porosity, which can be achieved by low W/C ratios and by using additions.

Degradation of the Concrete Itself

Expansive reactions inside the concrete that may lead to cracking and deterioration have the following causes: internal sulphate attack, external sulphate attack, alkali-aggregate reaction and free lime hydration.

The first two are due to sulphate action, which can have internal or external origins respectively. The presence of sulphates inside the concrete, linked to alkalinity and humidity and, most of all, high temperature inside the concrete during its early stages, leads to the formation of delayed ettringite inside the concrete, a process commonly known as DEF (delayed ettringite formation). Unlike the ettringite formed during the cement hydration reactions in their plastic phase, this ettringite is formed within already hardened concrete and, due to its expansive character, causes cracking to occur. There are no efficient ways to recover a structure affected by sulphate-induced expansive reactions, which lead to cracking in the concrete in a random fashion, and preventative measures should be taken to avoid this anomaly. In accordance with the specification LNEC E 461 "Concrete. Methods to prevent internal expansive reactions", these measures involve controlling concrete's maximum temperature; controlling concrete's alkali, aluminium and binder sulphate content; controlling humidity and keeping concrete in a relatively dry state; or controlling the calcium hydroxide content.

Alkali-aggregate reactions, also known as alkali-silica reactions (ASRs), are another cause of concrete degradation through expansive internal reactions. The expansive products are the result of alkali reactions, normally the cement reacting with the reactive silica in aggregates. In Portugal, this is a real problem and justifies the growing concern with working on this type of degradation. In concrete, it has the following mechanical consequences: occurrence of expansion pressure, formation of a network of inter-granular fissures, lack of cohesion at the cement paste/aggregate interface and altered mechanical characteristics. The most common macroscopic display of cracking is *craquelé* (random pattern) cracking, with efflorescence, frequently with a yellowish colour, as can be seen in Fig. 4.15.

The determining factors for ASRs are the presence of reactive aggregates, humidity and a highly alkaline paste. Controlling these factors is the best way to

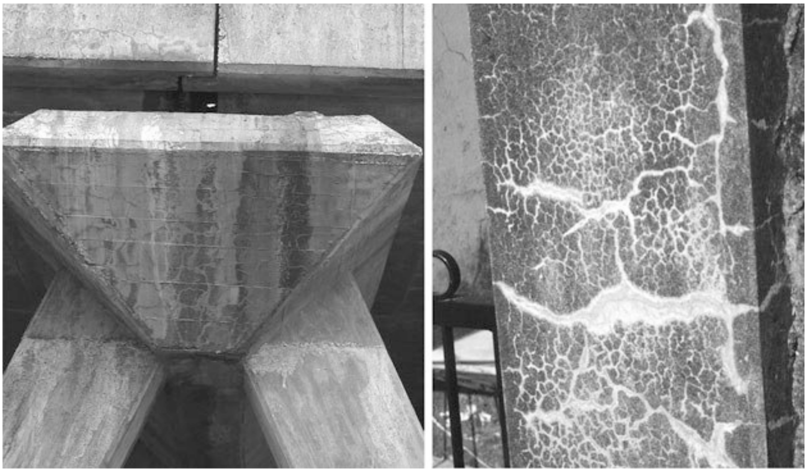


Fig. 4.15 Cracking caused by alkali-silica reactions

avoid degradation of the concrete. In accordance with LNEC E 461, aggregates with a reactive silica content of less than 2 % are considered to be nonreactive, calculated using petrographic analysis according to specification LNEC E 415 “Inert materials for mortar and concrete. Determination of potential reactivity with alkalis. Petrographic analysis”. As one of the determining factors for reactions is humidity, since reactions need a relative humidity of more than 80 %, the areas of the structure that are most sensitive are areas in contact with damp soil, walls exposed to the elements and areas with poor drainage or lack of waterproofing.

Free lime, which has not been slaked, tends to expand when it comes into contact with water. This phenomenon, when it occurs in concrete’s hardened state, may lead to degradation. However, controlling the free lime content in the different constituents of concrete makes this type of degradation rare.

Concrete shrinkage, when restricted, may cause cracking. Cracking, as well as affecting the appearance of the structure, can put the durability at risk when deep. Cracking that occurs due to concrete’s intrinsic behaviour may be classified as plastic, thermal or drying [23]. Plastic shrinkage is a particular case of drying and differs from it because it takes place during the plastic phase.

Cracking due to plastic shrinkage is common in slabs (Fig. 4.16), forming parallel diagonals, at around 45° to the corners of the slabs, distanced around 0.2–2.0 m, and may have a random pattern or follow the lines of the reinforcements. The main cause is quick drying of the surface, because of a lack of or inappropriate curing, producing concrete shrinkage at ages when it is still weak.

Thermal cracking takes place at young ages, since later the concrete will be strong enough to cope with this action. It arises from differences in temperature between different areas of a concrete element whose movement is restricted. It occurs most frequently in large volume elements restricted at the sides and is characterised by a linear orientation with equidistant fissures. There are no simple

Fig. 4.16 Plastic cracking crossing the entire slab

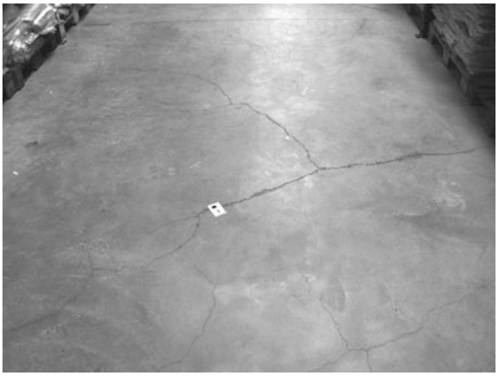


Fig. 4.17 Random drying cracking

recommendations for minimising the risk of this type of fissuring, since it can only be controlled with good planning of the concreting, for example, the location of construction joints, requiring coordination between the project designer and the builder.

Cracking caused by drying shrinkage occurs in the concrete in its dry state. All the constituents of concrete influence drying shrinkage, either individually or as the result of their interactions. Shrinkage is also affected by the temperature history, curing methods, environmental conditions and the relationship between the volume of the piece and its exposed surface. These cracks are characterised by being one-directional. Another type of cracking linked with drying shrinkage is random cracking. This is characterised by cracks that do not have an established direction, creating joined, irregular shapes (Fig. 4.17) that extend below the surface of the concrete and are generally caused when the concrete is young. It is also known as *craquelé*. Cracks opening may range from very fine cracks, almost invisible to the naked eye, up to a few tenths of a millimetre. Generally, random cracking may occur when the concrete was not properly cured and protected; the concrete was exposed to fast, prolonged drying on the surface; or it was subjected to exaggerated finishing action, leading to too much cement paste being drawn to the surface. This type of cracking should not be confused with the one caused by internal expansive reactions, since they take place at very different ages.

The most common chemical attacks arise from contact with water that has a low pH, aggressive CO_2, NH_4^+ or Mg^{2+}. Acidity in soil can also attack concrete. These aggressive agents tend to cause decalcification, which leads to disaggregation of the concrete. Decalcification is a general process in which, because of the lowered pH of the interstitial solution, the calcium found in compounds formed during cement hydration (such as calcium hydroxide and calcium silicate hydrates) is dissolved, leading to degradation of the structure formed by them.

The main action of microorganisms, in biological attack, as well as the aesthetic impact, is the decalcification of concrete, caused by the acids formed.

As well as accidental actions, the physical actions that are most common in concrete degradation are due to erosion by water. This erosion can be caused by cavitation or wear. Cavitation consists of erosion of the concrete by collapsing vapour bubbles generated in the water because of differences in pressure in areas where water flows at a high speed or falls with a great impact. Wear is essentially due to the mechanical action of particles dragged by water passing over the surface of the concrete. Erosion through abrasion should also be mentioned, although it is rarer. It consists of wear due to friction of the cement matrix and aggregates, occurring mostly because of wind action. Another physical action that may cause degradation of the concrete is freeze/thaw action, which leads to the formation of capillary stress in the pores of the concrete, creating microcracks and consequently new capillary spaces, continuing the degradation process with cracks up to the surface.

4.2.3.2 Characterisation of Properties Relating to Durability

The methods for characterising properties related to concrete's durability should take into account the causes and mechanisms that lead to deterioration.

In the case of the deterioration of concrete through corrosion of the reinforcements, the mechanisms are essentially related to transporting aggressive agents (chlorides and CO_2) inside the concrete, such as diffusion and permeability. The regulatory test methods provided for in specification LNEC E 465 to evaluate concrete durability are described in the following LNEC specifications: E 391 "Concrete. Determination of resistance to carbonation", E 392 "Concrete. Determination of permeability to oxygen" and E 463 "Concrete. Determination of the chloride diffusion coefficient by testing migration in non-stationary regime". Specification LNEC E 391 establishes the depth of carbonated concrete, over time, of a specimen subjected to an environment with high CO_2 content (5 %). In specification LNEC E 392, oxygen permeability is quantified by the oxygen flow that passes through a concrete specimen under different pressures. In specification LNEC E 463, an electric potential is applied to a specimen in contact with a chloride solution, forcing the diffusion of the ions to the inside of the concrete and determining the depth of penetration.

To decrease the potential for alkali-silica reactions, the reactivity of aggregates can be characterised by the accelerated test in a mortar bar, according to the American standard ASTM C 1260 "Standard test method for potential alkali reactivity of aggregates (mortar-bar method)", or reactivity of the concrete composition is estimated according to the procedures indicated in recommendation RILEM AAR-0 “Determination of alkali reactivity potential in concrete”.

4.3 Production, Application and Control

The following is quoted from the introduction to EN 206: “This European Standard defines tasks for the specifier, producer and user. For example, the specifier is responsible for the specification of concrete, clause 6, and the producer is responsible for conformity and production control, clauses 8 and 9. The user is responsible for placing the concrete in the structure. In practice there may be several different parties specifying requirements at various stages of the design and construction process e.g. the client, the designer, the contractor, the concreting sub-contractor. Each is responsible for passing the specified requirements, together with any additional requirements, to the next party in the chain until they reach the producer. In the terms of this European Standard, this final compilation is known as the “specification“. Conversely, the specifier, producer and user may be the same party (e.g. a contractor doing design and build). In the case of ready mixed concrete, the purchaser of the fresh concrete is the specifier and has to give the specification to the producer. This standard also covers the necessary exchange of information between the different parties. Contractual matters are not addressed. Where responsibilities are given for parties involved, these are technical responsibilities.”

4.3.1 Specifying Concrete

As quoted above, specifying concrete means establishing the requirements that concrete must meet, which may be behavioural or composition requirements. The specifier should bear in mind the following points: the use of fresh and hardened concrete; curing conditions; dimensions of the structure (heat development); environmental actions to which the structure will be exposed; any requirement for exposed aggregates or surface finishes; any requirement related to reinforcements cover or minimum cross-sectional width, e.g. maximum dimension of the coarsest aggregate; and any restrictions on the use of constituent materials with established suitability, e.g. arising from exposure classes.

EN 206 indicates how concrete should be specified in three different situations: *designed concrete*, which uses the strength and exposure classes indicated in the standard and some requirements for constituent materials as a reference (in this case, the producer is responsible for the concrete); *prescribed concrete*, whose responsibility lies with the specifier, indicating the composition requirements and respective constituents; and *standardised prescribed concrete*, if there is a corresponding valid standard, which is not the case in Portugal.

The most common way to specify concrete is the first one. In this case, the following elements are always indicated: exposure class; chloride content; maximum size of the coarsest aggregate; density class, for lightweight or heavyweight concretes; and consistency class. The elements, in this order, together with the references in EN 206, are used to identify the abbreviated form of a certain designed concrete, e.g. C30/37 XD2(P), C1 0.20, Dmax 22, D1.8 and S4.

4.3.2 Methods for Concrete Mix Design

Before the concrete is produced, its composition should be studied to define the proportion of each constituent, in order to respond to the pre-established requirements. This study, which begins by ascertaining the composition through analytical methods, will always have to be evaluated with experimental mixtures.

When designing the composition of concrete, the following factors should be taken into consideration: local availability of materials, appropriate workability for applying the concrete, adequate strength and durability in hardened state and minimising the final costs of the product. There is a range of good-practice rules that should be followed when studying concrete composition. They include regularly referring to the applicable standards, consulting all the parties involved in the construction, checking the properties of the concrete in different states, not establishing unrealistic demands, not establishing conflicting demands, not altering demands during the composition study and starting the composition study early enough.

Among the many methods for establishing concrete composition, we can refer to those enshrined in American practice [24] and British practice [25] and the methods based on reference curves [26]. Recently, there has been development in computational methods applied to concrete mix design [27]. The most commonly applied methods in Portugal are based on reference curves. These methods assume that the optimal particle size in the composition is given by a specific curve, previously defined using experiments. The best-known curves are the Fuller, Bolomey, Joisel, Dreux and Faury curves, and the last one is the most used.

4.3.3 Concreting Operations

After mixing, which can be done on site or at a concrete plant, the concrete is transported to the place where it will be moulded into its final form. The different concreting operations include casting—the range of procedures necessary to place the concrete in the mould; compacting—an operation to optimise compaction of the concrete; curing—procedure performed to avoid water evaporating prematurely; and protecting—operation to protect the concrete from external actions.

As already mentioned, standard EN 13670 "Execution of concrete structures. Part 1: Common" establishes the demands for materials related to the execution of structures, covering the above-mentioned operations.

4.3.3.1 Casting

Before the concrete is cast, some preliminary operations should be performed, specifically cleaning detritus, snow, ice and water from the moulds, checking the cover and planned position of the reinforcements and dampening the surfaces to be concreted.

While the concrete is cast, some basic demands should be respected, such as depositing the concrete continuously and as closely as possible to its final position; preserving the quality of the concrete, avoiding alterations in the composition on site, for example, not adding water and maintaining the water/binder ratio, consistency, homogeneity, among others; properly compacting the concrete (e.g. avoiding excessive horizontal movement); maintaining appropriate casting ability so that layer lines and excessive plastic settlement are avoided; keeping reinforcements embedded in the concrete, in accordance with the cover tolerances; and choosing equipment appropriate for concrete.

When concreting horizontal elements, such as slabs, it is recommended that casting begins from one corner, with the concrete unloaded onto previously placed concrete. Concrete should also never be unloaded in separate piles to be levelled later, or in large amounts to then be moved into its final position with a pocket vibrator. These practices normally lead to segregation, causing the mortar to move in front of coarse aggregates.

Correct concreting of walls is performed by placing the concrete in horizontal layers with uniform thicknesses of 15–50 cm. Each layer should be compacted before the following layer is applied. Drop height must be limited to around 1 m so that the concrete does not segregate, creating “honeycombing”, and so as not to damage the moulds.

Concrete can be placed through unloading (truck, bucket) or pumping. The latter is one of the most common processes, as it is versatile and allows the concrete to be cast at great distances from its arrival point. For the concrete to be pumped, it is recommended that it has good segregation resistance and low initial bleeding. In order to ensure this, the dosage of fine aggregates must be sufficient (around 380 kg at least for elements sized smaller than 80 μm); the fineness modulus of the sand should be between 2.2 and 2.5; the ratio between coarse and fine aggregates should be low; it is not advisable to have a maximum aggregate size that is greater than 1/4 of the tube diameter; it is recommended that appropriate admixtures are used to mitigate bleeding and allow for practical usage time.

4.3.3.2 Compaction

Except for self-compacting concrete, once placed in the mould, it is necessary to compact the concrete to obtain a higher density, expelling accumulated air and therefore lowering porosity, with better mechanical strength and durability. Compaction also makes it easier to lay the concrete on site, allowing for better filling of the moulds, better moulded surfaces (without voids) and good adherence between the concrete and reinforcements.

Defective compaction leads to honeycombing, streaks, layer lines, pores and excess voids, placing lines and cracking. Excessive compaction may lead to

Fig. 4.18 Casting and compaction

segregation of the concrete. There are internal compaction methods (e.g. using pocket vibrators) and external compaction methods (e.g. formwork vibrators, surface vibrators, compression rollers). The most common compaction method for regular concrete is pocket vibrators, as shown in Fig. 4.18. These vibrators transmit vibrations to the concrete, moving its finer particles, which leads to a behaviour that is more like a fluid.

In multilayered concrete, the vibrator should penetrate the previous layer (which should not yet be rigid) vertically and systematically at regular intervals. Layer thickness should not be more than the length of the vibrator needle. When concrete is placed on an inclined surface, it should begin to be placed at the bottom, so that compaction increases with the weight of the concrete added later, and vibration should take place in the same way as for multilayer concrete.

4.3.3.3 Curing

After setting, concrete continues to gain strength, provided that it does not lack the water necessary for hydration reactions to continue. The different methods used to inhibit water from evaporating from the mixture constitute curing. Curing the concrete is therefore the last of the important concreting operations and is indispensable.

Concrete at a young age should be cured to minimise plastic shrinkage, to ensure appropriate strength and durability in the surface area.

Anomalies linked to a lack of curing may be visible or invisible. Among the visible anomalies, we find surface cracking of the concrete due to plastic shrinkage and the occurrence of a surface with low abrasive strength, and low adherence of the cover (disaggregating surface and presence of powder). Invisible effects include high porosity of the concrete cover, with reduced ability to protect reinforcements, reducing concrete’s durability and also strength.

As mentioned, plastic shrinkage is drying shrinkage that takes place in the phase before the concrete hardens. It is more common in horizontal elements because of the larger exposed area. Aggravating factors for plastic shrinkage include intense drying (low relative air humidity, high air temperature, wind, high temperature of the concrete); reduced bleeding and low W/C ratio; and slow-setting concrete, due to the type of cement, use of additions (slag, fly ash) or admixtures with a setting delay effect.

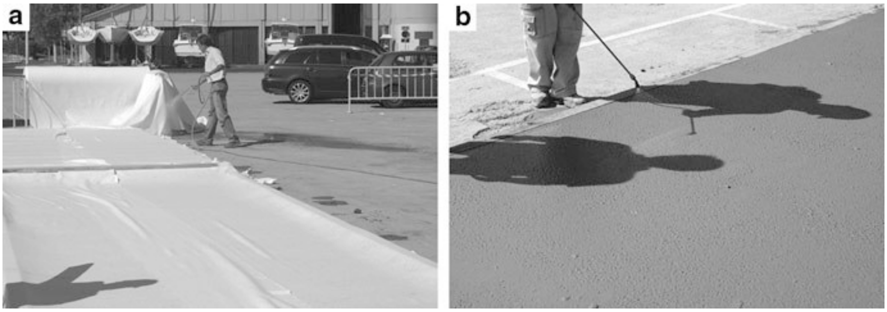


Fig. 4.19 Curing applying a wet covering (**a**) or curing membrane (**b**)

Table 4.12 Curing classes

	Class 1	Class 2	Class 3	Class 4
Time	12 h	–	–	–
% f_{ck28}	–	35 %	50 %	70 %

Curing methods are distinguished by providing additional supply of water or by sealing the concrete. The additional supply of water may come from flooding or immersing, spraying or misting, or even using wet covers (Fig. 4.19a). Sealing the concrete may be done by keeping the formwork, placing impermeable covers over the concrete or applying a curing membrane (Fig. 4.19b).

According to EN 13670, the duration of curing should depend on the development of concrete properties in the surface area. This development is described in terms of curing classes. These classes should be prescribed in the technical specifications for the execution project and are defined by the duration of curing or by the concrete's strength level, depending on the percentage of its characteristic strength at 28 days (% f_{ck28}), as shown in Table 4.12. In Annex F of EN 13670, curing duration times are recommended for classes 2–4, to be used if the strength of the concrete cover cannot be estimated.

Protection

In certain circumstances, specifically involving concreting in cold weather or for architectonic concrete, the concrete should be protected to mitigate the risks of freezing and harmful impacts or effects.

If, at an early age, the concrete requires protection against aggressive agents (e.g. chlorides), these demands should be established in the execution specification.

4.3.4 Controlling and Checking Conformity

As mentioned in the section on the regulatory framework, it is compulsory to control the production and conformity of all concrete structures made on site, prefabricated structural products, buildings and civil engineering structures.

Table 4.13 Conformity criteria for compressive strength

Production	Number of results from tests in the group	Criterion 1	Criterion 2
Initial	3	$f_{cm} \geq f_{ck} + 4$	$f_{ci} \geq f_{ck} - 4$
Continuous	≥ 15	$f_{cm} \geq f_{ck} + 1.48\sigma$	$f_{ci} \geq f_{ck} - 4$

Controlling production includes all the measures necessary to keeping the properties of the concrete in conformity with the specified requirements.

Controlling conformity can be established as the evaluation performed by the producer to check that the product satisfies the specified requirements, and is an integral part of production control.

For concrete, EN 206 establishes sampling plans and criteria for controlling conformity, and there are several properties that can be evaluated. Nonetheless, characteristic compressive strength (f_{ck}) is always controlled. As defined in EN 206, characteristic strength is the strength level below which it is hoped only 5 % of the possible results occur, representing the volume of concrete in question. When calculated using 28-day-old specimens, it is the value considered in identifying the concrete's strength class, e.g. C20/25 represents concrete with 25 MPa, characteristic strength obtained in cubes with 15 cm sides, or 20 MPa if the specimens are cylinders with 15 cm diameter and 30 cm height.

In accordance with EN 206, conformity of the compressive strength of concrete is evaluated using specimens tested at 28 days for average (f_{cm}) for groups of "n" non-overlapping or overlapping consecutive test results (criterion 1) and each individual test result f_{ci} (criterion 2). Conformity is confirmed if both the criteria given in Table 4.13, reproduced from Table 4.14 of EN 206, for either initial or continuous production are satisfied.

Portuguese Executive Law No. 301/2007 provides for compulsory checking of compressive strength of concrete by the user, in general, using identity tests in accordance with EN 206. Identity tests may be considered as tests upon receipt. They are carried out by the user or the specifier and are compulsory for concrete applied to regular structures. The main goal of the tests is to check if a certain volume of concrete is in accordance with the specifications. The specifier or user can also use identity tests for strength to check that the concrete in a structural element or series of elements belongs to a conforming batch, i.e. to ascertain if it is acceptable or not. The identity checking criteria for compressive strength are established in Annex B of EN 206.

4.3.5 Concrete Defects Linked with Concreting

There are several defects that can occur in concrete caused by problems during or after concreting. Among the defects that arise from concreting problems, further to casting, compaction, finishing and curing operations, those caused by the concrete's composition should also be considered. Defects relating to causes that occur after

Fig. 4.20 Stains caused by spilt paste and segregation of fine aggregates

concreting are discussed in Sect. 4.2.3.1 and refer to degradation mechanisms related to the concrete's durability.

Below, the most common defects caused by problems related to concreting operations are presented, and the factors that may cause them are identified.

4.3.5.1 Discolouration

This defect affects the aesthetic qualities of the concrete's surfaces and is characterised by a surface colour that is different from the one desired. This defect may arise in the form of colour variations in large areas of the surface, stains or darker spots or efflorescence (salts). The largest variations in colour may be due to alterations in the composition or characteristics of the constituents and also segregation of the finer materials because of inadequate vibration. Dark stains may occur due to local humidity variations through the formwork, spots on the formwork, spoiling the surrounding areas, through spilt paste, reduced cover or because of corroded reinforcements. Efflorescence consists of crystallised salt deposits that appear on the surface of the hardened concrete and that arise from water circulating through the material. In an initial phase, there may be deposits of calcium hydroxide on the surface of concrete with high bleeding (Fig. 4.20).

4.3.5.2 Blistering

Blisters appear as a localised raised section in the fine layer of the horizontal surface of concrete, arising during or shortly after the finishing operations. This defect is formed immediately below the surface of the concrete when water tends to bleed or when air cannot escape from the concrete. Blisters tend to form under the following circumstances: the surface, when the concrete is placed, has a lower temperature because of non-uniform setting of the laid concrete; the vibration used was not sufficient or was excessive; the surface of the concrete was prematurely sealed, due to inadequate finishing procedures; the environmental conditions cause fast water evaporation at the surface, erroneously causing the appearance that the bleeding period had finished; the concrete is thick, resulting in long periods necessary for

Fig. 4.21 Blisters on the surface of the concrete

water and air blisters to rise; a surface hardener was applied prematurely; the concrete is over a vapour barrier (Fig. 4.21).

4.3.5.3 Delamination

Delamination is similar to blistering and takes place when air and water are trapped on the surface, leading to detachment of portions of mortar, with thicknesses up to 5 mm. The main cause of delamination is a surface finishing applied when the concrete is still bleeding. Delamination tends to occur when factors that may lead to increased bleeding time (e.g. cold substrate) are present together with high ambient temperature.

4.3.5.4 Bugholes

Bugholes are small, regular (spherical) or irregular cavities that normally do not exceed 15 mm in diameter and are the result of air bubbles trapped on the surface of moulded concrete during laying and setting. Bugholes appear as small voids in the moulded surface of the concrete. These defects are typically caused by the presence of small air bubbles that are not removed during compaction of the concrete or by the use of an improper dismantling fluid that stops the bubbles rising. Bugholes tend to form when the concrete was not properly compacted; the vibrators were not properly spaced or their action areas did not overlap, leaving poorly vibrated areas; the dismantling fluid is inadequate; or the concrete has a very cohesive and viscous consistency (Fig. 4.22).

4.3.5.5 Sand Streaking

This anomaly is characterised by a texture similar to that arising from percolation of a liquid on a surface, such as can be seen at low tide on muddy beaches. The direction of flow tends to be random and seeks the path of least resistance, dragging fine aggregate with it and leaving well-defined streaks. Percolation arises when a less dense fluid (slurry) is able to run through the aggregate skeleton. This takes place when the formwork is not waterproof or when there is excess vibration. In the

Fig. 4.22 Bugholes

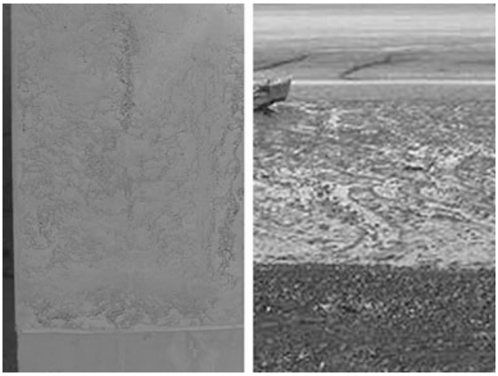


Fig. 4.23 Formation of sand streaks on the surface of concrete

former situation, slurry runs through openings in the formwork, dragging with it fine aggregate and forming grooves that are only visible after the formwork has been removed. Excess vibration causes segregation, which leads the fluid part of the concrete to rise, producing stains and grooves. The larger the area of excessive vibration, the more widespread the visual effect (Fig. 4.23).

4.3.5.6 Dusting

Dusting is the appearance of dust on hardened concrete, caused by disintegration on the surface. It tends to appear if a finishing operation is performed when bleeding water is still found on the surface of the concrete, leading to a high W/C ratio and therefore lower strength. This anomaly can also occur if appropriate curing is not performed, since this weakens the surface of the concrete, or if there is no protection against intense wind, rain or cold action is applied after finishing (Fig. 4.24).

4.3.5.7 Scaling

This defect consists of small, flat flakes of the concrete's surface becoming detached. Scaling begins with a small portion of the surface that separates from the rest of the concrete, normally because of freeze/thaw action. Over time, these

Fig. 4.24 Dusting

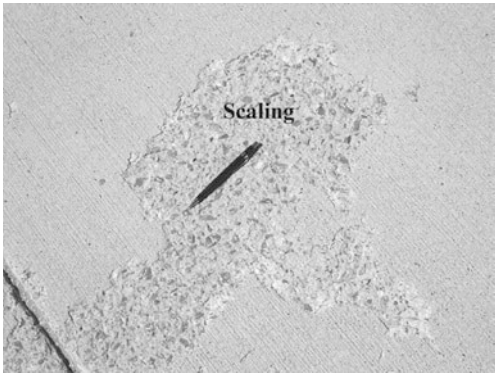


Fig. 4.25 Medium scaling

portions may get larger and join surrounding sections, producing large scaled areas. Scaling tends to occur if concrete is not resistant against freeze/thaw action, if it has not been properly cured or if the finishing operations were performed when bleeding water is still ongoing. Laying concrete in adverse environmental conditions (intense heat, cold or rain, etc.) may also lead to scaling on the surface (Fig. 4.25).

4.3.5.8 Honeycombing

Honeycombs are voids in the concrete caused by a lack of mortar using coarse aggregate agglomerates. This defect normally occurs when the concrete segregates because of an obstruction blocking flow when the concrete is laid, an excessive drop height, high reinforcement density or because of paste escaping from the formwork. It also tends to happen because of the following circumstances: difficult access to lay the concrete, making it necessary for the concrete to cover large distances; difficulty in vibration because of high mortar density or the distance between the access point and the concrete; high ratio between the maximum aggregate size and reinforcement spacing; and the concrete not properly studied for workability requirements.

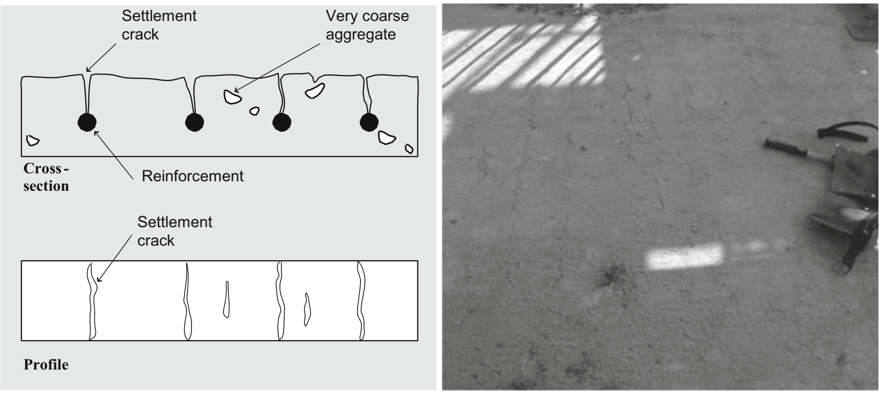


Fig. 4.26 Diagram showing plastic settlement cracking

4.3.5.9 Plastic Settlement Cracks

Defect evidenced by cracking is caused by restrictions on concrete settlement. Most concrete, after being casted, bleeds, that is, water rises to the surface so the denser particles settle. This phenomenon is more pronounced, the greater the height of the concrete element. As settling takes place in a phase when the concrete is still fresh, it is normally known as plastic settlement. If there are no restrictions to settling, the result is simply a lower surface level. However, if there are rigid elements, for example, reinforcement bars, restricting movement of the concrete settlement, it is possible for cracks to occur above the object causing the restriction (Fig. 4.26). Plastic settlement cracks may be prevented in three ways: reducing bleeding and settling, reducing restrictions to settling and using the revibration technique.

Layer Lines

Layer lines are lines visible on the surface of the concrete that show the separation between consecutive concrete layers. These lines are caused by premature setting of the lower concrete layer and inadequate penetration of the vibrator into the layer. They can also be caused by the use of a binding mortar between layers of concrete.

4.4 Concrete and Sustainability

The concept of “sustainable development” was introduced in the final report of the Brundtland Commission (World Commission on Environment and Development, WCED) [28] in 1987 and was defined as “development that meets the needs of the present without compromising the ability of future generations to meet their own needs”.

Meeting social needs for housing and infrastructure in a sustainable way is one of the most important challenges facing the construction industry. From this perspective, many construction materials have a large impact on the local and global environment. This is particularly true for concrete, since it is the most commonly used material.

For several reasons, it is thought that the concrete industry is not sustainable. Firstly, it consumes large quantities of material extracted from nature (e.g. aggregates); secondly, the main binder is Portland cement, the production of which contributes to the emission of gases involved in global warming (world production of Portland cement represents approximately 5 % of all global CO_2) emissions; thirdly, many concrete structures suffer from a lack of durability, which has an adverse effect on the productivity of the resources used.

In order to increase the sustainability of concrete, so as to meet society's needs without compromising the future, the factors causing concrete not to be sustainable should be mitigated.

The use of recycled materials in construction is an extremely important issue this century, particularly the use of waste from demolition sites, which can be used to produce concrete, reducing the amount of natural aggregate used.

Using additions from industrial processes, such as fly ash and slag, to replace Portland cement reduces the amount of cement binder used. Reducing Portland cement production will reduce CO_2 emissions, energy consumption and the global warming rate. Using additions normally helps reduce costs, also leading to improved concrete properties. Developing new cements, based on clinker and using industrial by-products, or cements with low C3S content, that is, those produced using less energy, has been one of the paths followed to reduce the environmental impact of using Portland cement.

In order to estimate the environmental impact of a construction material, it is necessary to take into consideration every stage of the material's life cycle, including production, the construction stage, working life and demolition. Planning concrete projects, therefore, taking into account adequate durability and reusing materials after the structure's working life, is one of the factors that contribute to sustainability in using concrete.

4.5 Final Considerations

For concrete to meet the demands during its use, knowledge about its constituents, properties and usage processes must be extensive.

Further to cement, the essential binder needed to give concrete its properties, the factor that most influences concrete performance is water, in its role as a constituent and its contact with concrete after casting. A high water–cement ratio produces a more fluid concrete, which leads to greater porosity and a subsequent reduction in strength and durability. On the other hand, the presence of water after casting provides a good curing, which guarantees adequate strength and durability of the surface. Nonetheless, it is water action that in most cases leads to concrete degradation, allowing aggressive agents to be transported into the concrete, for example, or stimulating internal expansive reactions.

The durability of a reinforced concrete structure will be guaranteed if the requirements for the concrete's constituents and execution of the structure are met, along with the strength class. Among the requirements for constituents, the most relevant are the content and type of cement, as well as the water–cement ratio. The most important factor to consider during execution of the structure is concrete cover, seen as the main barrier to guaranteeing the integrity of the reinforcements.

Concrete's performance in service will depend on the demands for which it was prescribed, provided that appropriate control is enforced, from the choice of constituents to working life, particularly by applying Executive Law No. 301/2007, of 23 August 2007, and building rules.

By defining priorities in terms of using waste and by-products, another factor for the widespread use of concrete can be found: a more and more sustainable environmental impact.

References

1. Neville AM (1997) Properties of concrete, 4th edn. Longman, London, p 844. ISBN 0-582-23070-5
2. Mediaco—La définition de béton. Mediadico, tous les dictionnaires… simplement !. http://www.mediadico.com/ditionnaire/definition/beton/1 (consulted on 19 Jan 2010)
3. Stanley CC (1979) Highlights in the history of concrete. Cement & Concrete Association, London, p 44. ISBN 072101156X
4. Sousa CA (1988) Fabrico e Propriedades do Betão, vol 1, 2nd edn. LNEC, Lisbon, p 401
5. Vitrúvio—*Tratado de Arquitectura* (2006) (trans: Justino Maciel M. IST Press, Lisbon. p 454. ISBN 972-8469-43-8
6. Hewlett P (1998) Lea's chemistry of cement and concrete, 4th edn. Elsevier, Burlington, p 1092. ISBN 0-7506-6256-5
7. Moreira de Sa B.J, Le Béton Armé http://lib.ugent.be/fulltxt/RUG01/000/895/607/RUG01-000895607-1905-080_2011_0001_AC.pdf (consulted on 18 Aug 2014)
8. Gabrysiak F. Matériaux, Chapitre 4 Les Bétons. http://www.ac-nancy-metz.fr/enseign/batiment_pro/ressources/laboratoire/chapitre%20004%20-%20les%20Betons.pdf (consulted on 9 Feb 2010)
9. Grünewald S, Walraven JC (2005) The effects of viscosity agents on the characteristics of self-compacting concrete. In: Proceedings of the second North American conference on the design and use of self-consolidating concrete with the fourth international RILEM symposium on self compacting concrete. RILEM Publications, Chicago, USA
10. Ribeiro S (2004) Argamassas Cimentícias Modificadas com Polímeros: Composição e Características. PhD thesis, IST/LNEC, Lisbon
11. Vieira M (2008) Betões Autocompactáveis: Reologia do Betão no Estado Fresco. PhD thesis, IST/LNEC, Lisbon, p 346
12. De Schutter G et al (2008) Self-compacting concrete. Whittles Publishing, Dunbeath, p 296. ISBN 978-1904445-30-2
13. Aïtcin P-C (2001) Bétons haute performance. Ed. Eyrolles, Paris, p 683. ISBN 2-212-01323-X
14. Vieira M (2003) Betões de Elevado Desempenho com Agregados Leves: Durabilidade e Micro-estrutura. Master's thesis, IST/LNEC, Lisbon, p 217. ISBN 972-49-1988-9
15. Mcleish A (1994) Underwater concreting and repair. Butterworth Heinemann, Oxford, p 160. ISBN 0-340-54466-X
16. Levitt M (2007) Precast concrete: materials, manufacture, properties and usage. Taylor & Francis Group, New York, p 206. ISBN 041526846X

17. NP EN 14487-1 (2007) Betão projectado. Parte 1: Definições, especificações e conformidade. IPQ, Lisbon, p 41
18. Bettencourt Ribeiro A (2004) Betão Compactado com Cilindros: Composição e Características. PhD thesis, FEUP/LNEC, Lisbon, p 535. ISBN 972-49-1994-3
19. Macosko CW (1994) Rheology: principles, measurements, and applications. VCH, New York, p 550. ISBN 1-56081-579-1
20. Tattersall GH, Pfg B (1983) The rheology of fresh concrete. Pitman Books, London
21. Barnes HA, Hutton JF, Walters K (1989) An introduction to rheology. Elsevier, Amsterdam, p 199. ISBN 0-444-87140-3
22. Roussel N (2007) Rheology of fresh concrete: from measurements to predictions of casting processes. Mater Struct 40:1001–1012
23. Concrete Society technical report no. 22—non-structural cracks in concrete (1992). 3rd edn. The Concrete Society, Wexham, p 48. ISBN 0-946691
24. ACI 211.1-91—standard practice for selecting proportions for normal, heavyweight, and mass concrete. ACI manual of concrete practice, p 38
25. Teychenné DC, Franklin RE, Erntroy H (1997) Design of normal concrete mixes. Building Research Establishment. ISBN 9781860811722
26. Sousa CA (1988) Fabrico e Propriedades do Betão, vol 2, 2nd edn. LNEC, Lisbon, p 219
27. De Larrard F (2000) Structures Granulaires et Formulation des Bétons. OA 34. LCPC, Paris, p 414. ISBN 2-7208-2006-8
28. Brundtland Commission—report of the World commission on environment and development. [Online]. 96th plenary meeting of the UN (1987). http://www.un.org/documents/ga/res/42/ares42-187.htm (consulted on 5 Feb 2010)

Bituminous Binders and Mixtures

5

José Neves, António Correia Diogo, and Luís de Picado Santos

Abstract

The subject of this chapter is to present materials for construction and civil engineering that incorporate bitumen and bituminous binders in its composition to be used in waterproofing systems and pavements of transport infrastructures, e.g. roads and airfields. General properties of bitumen, bitumen binders and bitumen emulsions are described. Waterproofing systems and bituminous mixtures are the main materials regarding the use of bitumen and bituminous binders for main civil engineering purposes. In the case of bituminous mixtures, the composition, properties and main products and applications are presented in the perspective of their use in pavement layers. Surface treatments and other special products and applications are also included. The main technical requirements are related to the materials, techniques and equipments involved during the design, construction, maintenance, rehabilitation and recycling of these bituminous materials.

Keywords

Asphalt • Bitumen • Bitumen emulsion • Bituminous mixture • Pavement • Waterproofing system • Surface treatment

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M.C. Gonçalves, F. Margarido (eds.), *Materials for Construction and Civil Engineering*, DOI 10.1007/978-3-319-08236-3_5

5.1 Introduction

This chapter deals with bituminous binders and mixtures used in waterproofing systems and in pavements of roads, highways, airfields, etc.

A wide variety of bituminous materials are used in construction, each having its own distinctive characteristics. Technical, economic and environmental criteria must be taken into account when choosing suitable materials from each application. These materials are widely used in waterproofing systems (bridges, retaining walls, tunnels) and in courses of pavements for roads, urban streets, parking lots, as well as for airfields.

The pavement is a structure, composed of one or more courses, to assist the passage of traffic over terrain. Course is the structural element of a pavement constructed with a single material. Bituminous mixtures are currently used in pavement construction and maintenance, with respect to the following courses:

- The surface course, the upper course of the pavement which is in contact with the traffic.
- The binder course, the part of a pavement between the surface course and the base course.
- The base course, the main structural part of the pavement. The base may be laid in one or more courses.

A description of the general properties and types of bitumen and bituminous binders is presented.

Considering the most important applications, water proofing systems and bituminous mixtures are described in terms of building and construction in civil engineering. In the case of bituminous mixtures, products and applications are described for road and airfield purposes. Aspects related to maintenance, rehabilitation and recycling are also important taking into consideration the life cycle of the materials when in service.

Along this chapter, the requirements of bitumen, bituminous binders and bituminous mixtures are described strongly relying on the technical specifications valid for each application type according the European experience.

5.2 Bitumen and Bituminous Binders

5.2.1 General Properties

Bituminous binders are adhesive materials that contain bitumen, which may be in the form of conventional bitumen, modified bitumen or bitumen emulsion. Due to their properties, bituminous binders have a wide range of applications in civil engineering, most notably in the construction of waterproofing systems and in the paving of transport infrastructures.

The term “bitumen” refers to a material that is non-volatile, adhesive and waterproof which is derived from crude oil or present in natural asphalt. It is highly viscous, nearly solid at air temperature and soluble (completely or nearly completely) in toluene. Bitumen can be naturally occurring (from natural asphalt lakes and rock asphalt) or industrially produced.

The term “natural asphalt” refers to bitumen that occurs naturally in asphalt lakes and rock asphalt in general (including impregnated limestone, etc.). The earliest known use of natural asphalt dates back to the Middle Palaeolithic period (40,000 B.C.). Traces of natural bitumen used as an adhesive to join the head and handle of a scraper were found at Umm el Tlel, Syria [1]. The use of bitumen as a waterproofing agent is also very old. There is evidence of it having been used in ancient Assyria (2000–1000 B.C.) to waterproof cisterns, boats and water lines. Bitumen was also used as waterproofing in the Hanging Gardens of Babylon (one of the seven wonders of the ancient world) built during the reign of Nebuchadnezzar II (632–562 B.C.), as well as in the construction of ziggurats [2].

Later, materials from other sources with properties similar to those of natural asphalt were manufactured and used:

(a) Coal tar, which is distilled from bituminous coal—the residue from distilling the tar is coal tar pitch.
(b) The residue from distilling pine resin, which is known as colophony, rosin or Greek pitch.
(c) Petroleum bitumen, which is made from the residue of vacuum distillation of crude oil or a crude oil blend (“vacuum residue”).

The term “pitch” refers to the product used for caulking ships—the term is used to mean both black pitch and the lighter-coloured rosin.

There is some ambiguity in how the term asphalt is used. In the United States, the term “asphalt” refers to the product obtained from distilling crude oil (the vacuum distillation residue). In the British Isles, the same word “asphalt” means a mixture of petroleum bitumen and mineral aggregate. In France, the word “asphalte” also refers to the bitumen and mineral aggregate mixture.

As for chemical composition, bitumen is a complex mixture of aliphatic and aromatic hydrocarbons, both polar and non-polar, that form a complex, polycyclic system. As the estimated order of magnitude of the number of individual chemical components is about ten thousands, it is more convenient to describe bitumen in terms of families of components, defined according to suitable criteria. In most cases, criteria such as solubility in certain solvents have been adopted.

The chemical composition of naturally occurring bitumen depends on their geographic origin. The geographic origin of bitumen used in artefacts produced in ancient times could be determined from their chemical composition. Likewise, the chemical composition of petroleum bitumen strongly depends on the origin of the crude oil used, and on how the refining process is carried out [3].

The chemical analysis of bitumen is normally obtained by successive separations either by precipitation or by extraction, using selected sets of solvents according to different conventions [3–10]. The obtained composition in terms of "families" of components will obviously depend on the method chosen.

The first family of chemical components usually considered is asphaltenes. Precipitation of asphaltenes is one of the main causes of clogging in crude oil pipelines. Asphaltenes constitute the fraction of polar cyclic aromatic hydrocarbons with the highest molecular weight; they are insoluble in low molecular weight alkanes such as pentane, hexane and heptane [11]. It must be emphasised that, for any given bitumen the value of the asphaltenes fraction varies according to the solvent chosen (*n*-pentane, *n*-hexane or *n*-heptane). Not only the asphaltenes fractions are solvent dependent, but also the colour and other physical properties of the isolated asphaltenes are also solvent dependent. Therefore, there are chemical components which may or may not fall into the asphaltenes class, depending on the alkane chosen to perform the precipitation.

The second family of components is the maltenes [3, 12–17]. "Maltenes" are the bitumen fraction soluble in the *n*-alkane used to precipitate asphaltenes. So, maltenes fraction is solvent dependent too. It should be stressed that maltenes are not exactly the same thing as "non-asphaltenes". Since the number of bitumen chemical components is very big, and since maltenes are separated from asphaltenes just by precipitation into a single solvent, it is very likely that some components of bitumen are split between the asphaltenes fraction and the maltenes fraction in variable proportions depending on the solvent used in fractionation. Maltenes include polar cyclic aromatic hydrocarbons of relatively lower molecular weight (as compared to asphaltenes) named "resins" [13], less polar aromatic unsaturated hydrocarbons (alkenes and dienes) named "aromatics" and non-polar saturated hydrocarbons (straight-chain alkanes or *n*-alkanes, isoalkanes and other branched-chain alkanes and cycloalkanes) that constitute the "saturates" fraction [12]. In the nomenclature of oil industry, alkanes are named paraffins, cycloalkanes and their derivatives are named naphthenes, alkenes are named olefins and dienes are named diolefins.

The acronym SARA (Saturates, Aromatics, Resins and Asphaltenes) is widely used to assess the chemical composition of bitumen [4, 6]. Other classification systems are also often used. The Rostler-Sternberg classification method [17] (ASTM D2006) considers five families of components: asphaltenes (determined by precipitation in *n*-pentane), nitrogen bases, first acidaffins, second acidaffins and paraffins. In the modified Rostler-Sternberg classification system, the following six families of components are considered: asphaltenes (A), first nitraffins (N1), second nitraffins (N2), first acidaffins (A1), second acidaffins (A2) and paraffins (P).

Bitumen structure was pictured for a long time as a colloidal system made up of micelles of asphaltenes dispersed in the maltene phase; on the other hand, in the maltene matrix, the resins are preferentially placed around the asphaltene micelles and stabilising the dispersion by this way ("peptising" the asphaltenes) [14–20]. These are the fundamental assumptions of the so-called "colloidal model".

However, neither it has been demonstrated that bitumen is a two-phase system nor experimental evidence exists that peptising actually occurs. Experimental evidence obtained by atomic force microscopy [21–24] puts the colloidal model

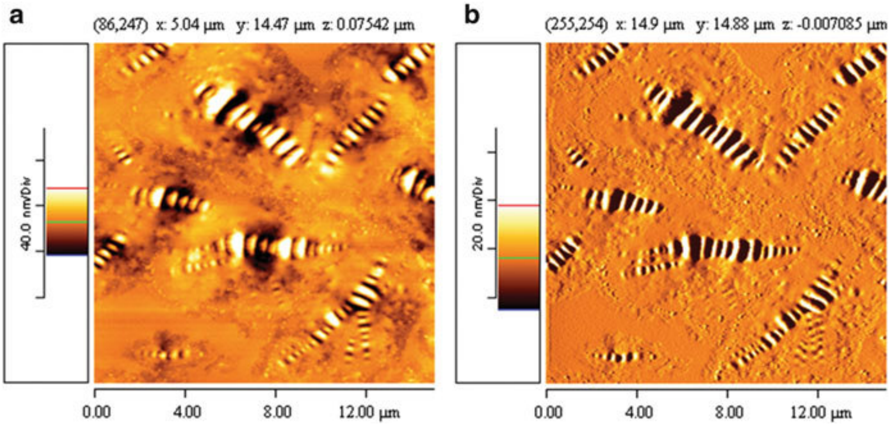

Fig. 5.1 Atomic force microscopy images of a 50/70 bitumen (tapping mode). (**a**) force modulation image (topographic mode); (**b**) phase shift image. Image size: 15 × 15 mm^2. Catana phase corresponds to bee-shaped formations; periphase surrounds catanae; paraphase does not surround catanae

into question with respect to both the number of phases in bitumen (three or four, instead of two) and their relative concentrations [24]. For example, according to the colloidal model, in a bitumen with 10 % asphaltenes, the micellar phase should occupy approximately 10 % of the total volume; however, the available experimental data does not support this assumption. Most probably, resins look more like mini-asphaltenes or the asphaltenes like maxi-resins, since there appears to be no obvious structural discontinuity between asphaltenes and resins. Atomic force microscopy images (Fig. 5.1) show that the catana phase (the dispersed bee-like structures) includes all the asphaltenes fraction and an important part of the resins fraction. The remaining components are distributed in the periphase (the phase that surrounds the catana phase) and in the paraphase (the continuous phase that surrounds the periphase) [21–24].

The microstructural complexity of bitumen has a strong influence in the rheological properties and rheological material functions of bitumen and bituminous materials [20, 25–27]. Bitumen is a viscoelastic liquid, and its rheological behaviour is strongly dependent on temperature, shear and extensional strain rates and time. At very high temperatures (160–180 ºC) bitumen behaves like an almost-Newtonian low viscosity fluid (viscosity is on the order of a few mPa.s). As the temperature drops, its rheological behaviour resembles the one of a shear-thinning non-Newtonian viscoelastic fluid (the viscosity decreases as shear rate increases) while at the same time the elastic components of the relevant material functions (shear modulus, shear compliance, etc.) are enhanced. At a few dozen degrees below ambient temperature, bitumen may present mechanical behaviour similar to that of a glass (organic). Several different relaxation processes probably coexist in a fairly narrow range of temperatures that are usually interpreted as “glass transitions”.

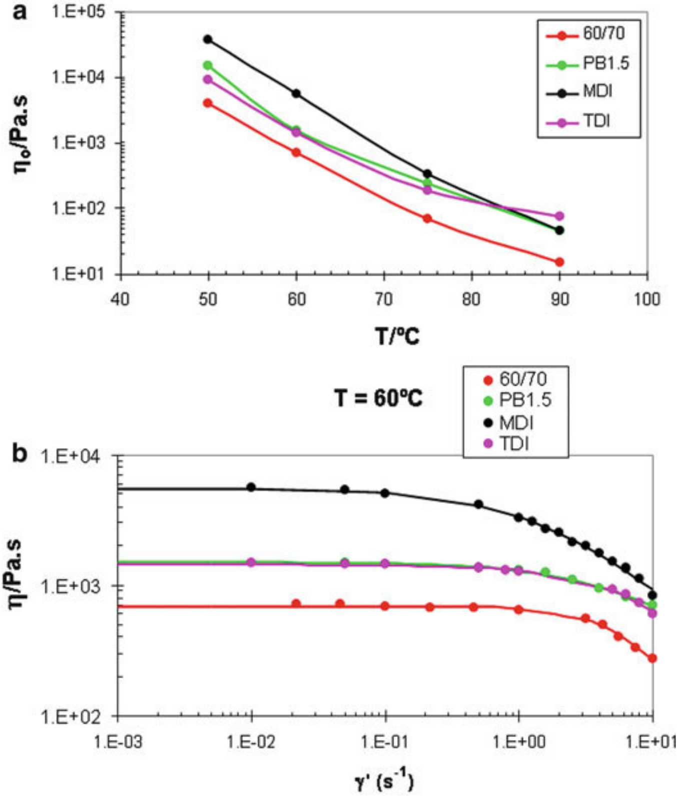

Fig. 5.2 (**a**) Temperature dependence of bitumen viscosity (60 °C); (**b**) Shear rate dependence of bitumen viscosity (60 °C). Labels: a) 60/70: conventional bitumen 60/70; b) PB1.5: bitumen 50/70 modified with SBS; c) MDI: bitumen 60/70 modified with MDI-polymeric; d) TDI: bitumen 60/70 modified with toluene di-isocyanate (TDI)

There is strong experimental evidence that bitumen is not thermo-rheologically simple, i.e. that time-temperature superposition principle does not hold. These results are not surprising. Time-temperature superposition in rheological material functions (viscosity, moduli, compliances, etc.) is observed if and only if all the relaxation times (or the full relaxation spectrum) exhibit the same temperature dependence. Given the complexity of bitumen, it would be truly surprising that the relaxation or retardation spectra of the thousands of components found in bitumen should present exactly the same temperature dependence (Fig. 5.2a, b).

Bitumen is usually classified by determination of the penetration index [S-1]. This test is done at 25 °C and consists of inserting a standard needle into a bitumen sample under a constant load of 100 g-force (1.02 N) for 5 s. The penetration index or, more simply, penetration, is the penetration depth of the needle, expressed in

Table 5.1 Characteristics and grades of paving bitumens most commonly used in paving work (adapted from [33])

Characteristic	Test method	Classes	
		35/50	50/70
Penetration at 25 °C	EN 1426 [S-1]	35–50	50–70
	ASTM – D5/D5M [S-1a]		
Softening point	EN 1427 [S-4]	50–58	46–54
	ASTM – D36/D36M [S-4a]		
Change of mass (RTFOT) (%)	EN 12607-1 [S-6]	≤0.5	≤0.5
	ASTM D6521 [S-6a]		
Retained penetration (RTFOT) (%)	EN 12607-1, Annexe A [S-6]	≥53	≥50
	ASTM D6521 [S-6a]		
Increase in softening point (RTFOT) (ºC)	EN 12607-1 [S-6]	≤11	≤11
	ASTM D6521 [S-6a]		
Flash point (ºC)	EN ISO 2592 [S-7]	≥240	≥230
	ASTM D92 [S-7a]		
Solubility (%)	EN 12592 [S-8]	≤99.0	≤99.0
	ASTM D5546 [S-8a]		
	ASTM D2042 [S-8b]		
Fraass breaking point (ºC)	EN 12593 [S-9]	≤−5	≤−8
Kinematic viscosity at 135 °C (mm^2/s)	EN 12595 [S-10]	≥370	≥295
	ASTM D2170/D2170M [S-10a]		

tenths of a millimetre. The penetration index is related to consistency and is one of the most commonly used properties in classifying bituminous binders.

The various grades of conventional bitumens are defined according to upper and lower limits of the penetration index: bitumen 35/50 has a penetration index between 35 and 50 tenths of a millimetre. Table 5.1 shows the main characteristics and grades of the bitumens most commonly used in paving work [33, S-2, S-3, S-3a]. Within each class, other properties that are important for characterising bituminous binders are also considered, such as softening point [S-4] and viscosity [S-5, S-5a].

The composition of bitumen undergoes changes since the application on the worksite to the end of its useful life. The more volatile components (i.e. the lower molecular weight saturates fraction) volatilise, contact with the atmosphere and sunlight causes oxidation and photo-oxidation reactions; phase morphology may also change with time, so the main result of all these factors is an increase in the asphaltenes and resins contents and a decrease in the aromatics and saturates contents.

The time evolution of bitumen properties, known as ageing, depends on its initial composition, the original type of crude oil used and the way it was refined, the thermal cycles suffered after leaving the refinery (modification, transport, production of a mixture at a plant, etc.) and the temperature and degree of exposure to atmospheric conditions on the occasion of the application procedures and during its in-service life [28, 29]. Aged bitumen is usually harder (with a lower penetration index) than fresh bitumen: bitumen hardening is one of the effects of ageing, due to changes in chemical composition. Aged bitumen can be rejuvenated. Rejuvenation is usually performed by correcting the composition and using appropriate additives.

In addition to the use of conventional bitumen in paving, it is also possible to modify bitumen properties by incorporating other chemical substances called modifiers. By this way, modified bitumen is produced with specific properties that make it suitable for given applications.

Modified bitumen falls into three main categories: modified binders, bituminous binders with additives and special bitumen [30].

Modified binders result from the addition of polymers and other chemical agents to conventional bitumen. The microstructure of bitumen is substantially changed as well as its physical and mechanical properties. Modified binders are prepared (blended) before application on the work site, either in dedicated plants or in a special mobile unit. The modified binder may therefore be tested and evaluated before use. It must be noted that characterisation and classification of modified binders is a complex and specific task, and it cannot always be done by using the traditional indicators for conventional bitumen.

Modified bitumen is usually classified as follows [31]:

1. Bitumen modified with natural or synthetic rubber.
2. Bitumen modified with crumb (recycled) rubber.
3. Bitumen modified with thermoplastics: polyolefins like polyethylene, polypropylene, atactic polypropylene, olefinic thermoplastic copolymers and others.
4. Bitumen modified with block copolymers, e.g. styrene-butadiene (SB), styrene-butadiene-styrene (SBS), ethylene vinyl acetate (EVA) and others.

A new class of modified bitumen was recently introduced [24–27]:

5. Bitumen modified with reactive polymers (poly-isocyanates, polyurethanes, polyureas and others).

In the first two cases, the bitumen is modified by adding cured (cross-linked) elastomers. During the blending process, the bitumen components with greater affinity to the rubber penetrate the crumbs, causing them to swell: the final result is a suspension of swollen granules in the bitumen. In the third case, the bitumen is modified with thermoplastics (also known as plastomers); they are expected to incorporate preferentially the phases more rich in saturates. In the fourth case, the bitumen is modified with thermoplastic elastomers; the different blocks of block copolymers are expected to be distributed among bitumen phases according to the polarity of the blocks. In all these cases, the modifier is not soluble (thermodynamically soluble) in the bitumen. As a result, the blending process is rather complex, requires an appropriate blender design and several hours of mechanical work at temperatures on the order of 170–190 °C. The product obtained has a multiphase texture and it is not in thermodynamic equilibrium; segregation of some of the components may occur, if it is not taken enough care when handling these materials. Segregation is prevented and minimised by the use of bitumen modified with reactive polymers.

In general, modified bitumen presents higher viscosity, higher softening point, and lower Fraass temperature than the corresponding conventional (unmodified) bitumen. Modified bitumen is also less sensitive to temperature variations, and is more cohesive. Best cohesive strength is found for bitumen modified with reactive polymers [32].

Comparing the effects of using plastomers or elastomers to modify bitumen, plastomer-modified bitumen shows higher viscosity at ambient temperature, making it harder and with a higher softening point as compared to elastomer-modified bitumen. Consequently, plastomer-modified bitumen is comparatively less workable. On the other hand, elastomer modification confers greater flexibility and malleability to the binders, both at high and low temperatures.

Bituminous binders with additives are obtained by incorporation of the additives during the mixing process. In contrast to modified binders, the effect of the additive on the bituminous binder can only be assessed directly in the already-manufactured bitumen blend or surface coating. The additives used in bituminous binders can be of various types and natures. The most common ones are polymers of different kinds, recycled plastic materials, crumb rubber, fibres, natural bitumen and asphalts [30]. Natural organic fibres or manufactured fibres may also be added to bitumen. Manufactured fibres may be synthetic (e.g. polyester, polyethylene, polypropylene and acrylic), mineral (fibreglass, ceramic fibres, stone wool) and metallic (stainless steel, steel wool). In general, fibre-reinforced bitumen is more adhesive and more flexible, which improves the ageing resistance.

Generally speaking, modified bitumen mixtures are used either in original construction or in maintenance works that require properties that cannot be achieved with traditional bitumen. This is the case of modified bitumens and modified bitumen emulsions used in surface coatings, cold-set bitumen micro-agglomerates, high modulus bitumen blends, asphalt mortars, porous asphalt and rough microconcrete, and asphalt concrete.

Special bitumen is the result of special crude oil refining processes. It is manufactured to meet the requirements of very specific applications, which in some cases are not covered by the usual standards or specifications. The special bitumen most commonly used in road paving is hard bitumen (with penetration index of less than 25 tenths of a millimetre), pigmented bitumen, binders and special emulsions.

Efficient pumping of bitumen requires a low enough value of the viscosity; heating is the most common procedure to lower the viscosity as required. In addition to heating, emulsification and dissolution in solvents are other possible techniques; they give origin to bitumen emulsions and cutback bitumen, respectively. Fluidification of bitumen is a technique that is rarely used today, due to safety concerns.

The bituminous binders currently used in construction can be categorised as follows:

- Conventional bitumen (from direct distillation of bitumen).
- Modified bitumen.
- Hard bitumen.
- Special bitumen modified with recycled tyre rubber.
- Emulsified conventional bitumen (bitumen emulsion).

5.2.2 Bituminous Binders

Conventional bitumen, traditionally used in paving, is the residue from vacuum distillation of crude. Crude oil is first separated into fractions by fractional atmospheric distillation, in oil refineries. The residual bottoms from atmospheric distillation are further distilled at low pressure (vacuum distillation). The residue from the vacuum distillation may be further changed by "air-blowing" to more or less extent: the final result is bitumen. Fully blown bitumen or oxidised bitumen is suitable for roofing purposes, as well as for flooring mastics and coatings. Air-rectified or semi-blown bitumen is suitable for paving purposes. In addition to serving as the raw material for producing other types of bituminous binders (see below), air-rectified bitumen is used extensively in the manufacture of various types of hot mix asphalt (HMA) and are widely used in road construction for surface, binder, and base courses.

Currently, a bitumen for paving must comply with the requirements set out in EN 12591 [S-2], which specifies the properties and the respective testing methods to be used for characterising this type of bitumen. As mentioned above, Table 5.1 shows the main classes of conventional bitumen that are most often used in paving work.

The modified bitumen most commonly used in construction is either hard bitumen or bitumen modified with recycled tyre rubber. Modified bitumen is specified by EN 14023 [S-11] (and ASTM D6154 [S-11a]). Modified bitumen is used when some properties of bitumen blends need to be changed, e.g. flexibility and temperature sensitivity. Modified bitumen is used in the production of open-type or thin bitumen blends, such as porous asphalt and rugous asphalt concrete for thin and ultra-thin surface courses.

Hard paving bitumen is used to produce the so-called high modulus bituminous mixtures, which are used in base course applications. The characteristics of these types of bitumen are set out in EN 13924 [S-12] (and ASTM D946/D946M [S-12a]).

Special rubber-modified bitumen is produced by adding crumb rubber from recycled used tyres to conventional bitumen. It is used primarily to make porous, open and rugous asphalt mixtures that act as an anti-cracking interface, or bitumen mortars made with modified bitumen, which can be of three types: low viscosity, medium viscosity or high viscosity bitumen.

Low viscosity bitumen is modified with crumb rubber at a concentration of less than 8 % (w/w). In medium viscosity bitumen, the corresponding percentage of incorporated crumb rubber is 8–15 % (w/w). The low viscosity and medium viscosity modified bitumen with recycled tyre rubber both present suitable storage stability.

High viscosity bitumen, on the other hand, is modified with crumb rubber at a concentration of more than 18 % (w/w). Bitumen with such a high percentage of recycled tyre rubber has low storage stability; in situ preparation at the work site is mostly required. The basic bitumen to be modified is generally a conventional paving grade bitumen according to EN 12591 [S-8] (and ASTM D5546 [S-8a]), and it is selected based on the characteristics required for the project. The crumb rubber used in this modified bitumen is obtained from recycled tyre rubber (100 % vulcanised). This bitumen is produced in special reactors at bitumen plants: some bitumen components (the lighter fractions) penetrate the rubber network which becomes swollen up to some extent. The reduction of lighter fractions in the bulk bitumen due to rubber swelling produces some stiffening of the continuous bulk bitumen matrix; it is compensated by addition of aromatic oils and/or naphthenes at low percent (w/w) that soften the bitumen matrix to the required level.

When choosing the best type of bitumen for a given application, performance as well as production and construction conditions are the most important requirements to be taken into account. In the case of bitumen blends, for example, the choice of the best bitumen blend strongly depends on the structural and functional performance required for the mixture when it is applied to the pavement, and on the traffic and weather conditions which it will undergo. Low penetration grades of bitumen are often recommended for areas subject to high summer temperatures since they are less temperature sensitive.

5.2.3 Bitumen Emulsions

A bitumen (asphaltic) emulsion is a (direct) emulsion of bitumen in water. The dispersed phase consists of bitumen droplets and the continuous phase consists of water. These emulsions are not thermodynamically stable. “Stabilisation” of the emulsion is nothing more than a set of procedures to prevent disruption processes (emulsion breakdown) and to extend the shelf-life of the emulsion. The disruption processes may include:

(a) Sedimentation, if droplet density is greater than the density of dispersed phase.
(b) Creaming, if the density of the bitumen droplets is lower than the density of the water phase.
(c) Flocculation of the particles of the dispersed phase.
(d) Coalescence of the droplets of the dispersed phase.

In general, “stabilisation” is achieved through the combined effects of surfactants to decrease the interfacial tension between water and bitumen, thereby reducing the size of the droplets; ionic compounds that increase the electric charge of the emulsion droplets in order to produce electrostatic repulsion among them, thereby preventing coalescence; and additives to change the viscosity of the dispersed phase in order to reduce the mobility of dispersed phase droplets.

Some additives have multiple effects. For example, the use of ionic surfactants reduces surface tension and increases the electric charge of the dispersed droplets. This characteristic is used to classify bitumen emulsions into the following categories:

(a) Cationic emulsions: if the emulsifier contains, e.g. tertiary amines, the formation of substituted ammonium compounds on the surface of the dispersed droplets will give them a positive electrostatic charge.
(b) Anionic emulsions: if the emulsifier contains, e.g. carboxylic acids, substituted carboxylates will tend to settle on the surface of the droplets, giving them a negative electrostatic charge.
(c) Non-ionic emulsions: the emulsifiers are non-ionic and provide other mechanisms of stabilising the emulsion.

Bitumen emulsions must comply with EN 13808 [S-13] and ASTM D2397 [S-13a], which specify the technical requirements and performance classes of these products.

Emulsions are identified using an alphanumeric code that indicates the most important properties of cationic bituminous emulsions, namely the polarity of the bitumen particle, the nominal binder content produced from bitumen, the binder type and the breaking value. For example, an emulsion of “C 40 B 3” type is a classic cationic emulsion with a nominal binder content of 40 % produced from bitumen and a class 3 breaking value. There are two types of emulsions: classic and modified. Bitumen emulsions of each type are classified according to their ionic charge, bitumen content and breaking rate.

“Breaking” of an emulsion is the irreversible separation of its constituent phases, which are bitumen and water. Depending on their breaking rate, both cationic and anionic emulsions are classified as rapid, medium or slow breaking. The breaking rate depends on the type of emulsion, on the surface area of the aggregates and on their mineral composition.

Classic bitumen emulsions can be used in impregnation sprays, bond coat sprays, dust suppression sprays, curing sprays, surface coatings and cold-set or heat-set mixtures [33, 34], which will be discussed below under applications.

Bitumen emulsions for a given type of application should be chosen based primarily on the mineral composition of the aggregate, the cleanness of the aggregate and weather conditions.

5.3 Water Proofing Systems

The main goal of waterproofing systems is to seal a separating layer, usually a covering. A substantial number of waterproofing treatments involve application of bitumen using different methods [35–37]. A number of standards for water proofing systems may be found in references ([S-15] to [S-21]).

Typical methods of waterproofing include:

1. Asphalt shingles.
2. Bitumen felt underlayments.
3. Oxidised bitumen membranes.
4. Bitumen membranes made with modified bitumens.
5. Built-up roofing (BUR) systems.
6. Non-bituminous synthetic membranes (EPDM, PVC, TPO).
7. Waterproofing liquids.

Asphalt shingles consist of a fibreglass mat impregnated with a bituminous blend of oxidised bitumen and mineral fillers (such as limestone), coated with mineral granules on one side. Asphalt shingles are widely used in the United States, where they account for approximately 63 % of the market in terms of covered area. In Europe, however, they represent a very small portion of the market (<5 %) [36].

Bitumen underlayments can be considered the precursors of modern bitumen membranes. They are produced by impregnating organic felts with normal or oxidised bitumens, or with tar pitch. They are used in the United States under shingle and tile coverings. These are also not widely used in Europe.

Bitumen membranes are made of a reinforced felt paper impregnated with a bitumen blend, to which various types of surface finishes are applied. The bitumen blend is usually a polymer-modified bitumen with mineral fillers. According to the definition given in EN 13707 [S-14], ASTM D226/D226M [S-14a], ASTM D2626/D2626M [S-14b] and ASTM D2178/D2178M [S-14c], a reinforced bitumen membrane is a flexible layer of bitumen, incorporating one or two internal or external reinforcements. It is sold in the form of ready-to-use rolls. The rolls are one metre wide and vary in length (between 8 and 12 m) and in weight per unit of area (between 2.5 and 5 kg/m^2), with the total weight of a roll ranging between 36 and 40 kg.

Figure 5.3 presents a schematic constitution of a bituminous membrane (Imperalum).

In construction works, rolls are usually applied by one of three different processes:

1. Cold-applied at ambient temperature, using special adhesives.
2. Soft-applied, where the material surface is softened (by torch, hot air) in order to ensure good adhesion to the substrate.
3. Heat bonding, by applying preheated bitumen to the surface.

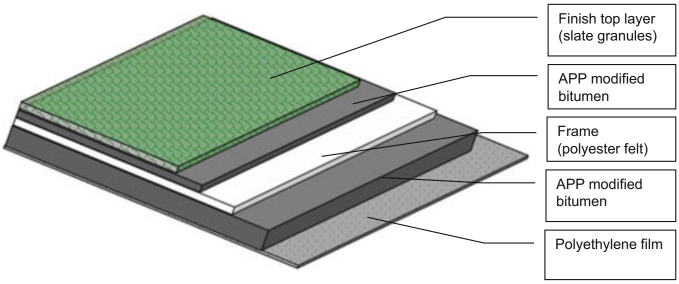

Fig. 5.3 Schematic constitution of a bituminous membrane with granular slate finish [37]

Various types of bitumen blends can be used to impregnate waterproofing membranes.

In oxidised bitumen membranes, the impregnating bitumen blends are made up of oxidised bitumen and mineral fillers (limestone, in particular). Bitumen oxidation is a process that changes the composition of bitumen, by increasing the concentration of polar components. For example, oxidation of bitumen with a given original composition in terms of asphaltenes, resins, aromatics and saturates promotes an increase in the concentrations of asphaltenes and resins and a decrease in the concentrations of aromatics and saturates. The increase in the polar components fraction improves adhesion and increases the viscosity. The use of oxidised bitumens has been on the wane for a number of reasons, in particular because of the possible generation of toxic chemicals due to the oxidation process used.

In modified bitumen membranes, the impregnating bitumen blends are made up of bitumen modified with thermoplastic elastomers or bitumen modified with thermoplastics. The most commonly used thermoplastic elastomers are styrene-butadiene-styrene (SBS) copolymers and styrene-ethylene-butadiene-styrene (SEBS) copolymers. As for thermoplastics, atactic polypropylene (APP), a sub-product of the polypropylene industry, is used almost exclusively. In fact, it is the only known application of APP [37].

Modified bitumen modified for use in waterproofing membranes has relatively high polymer concentrations (12 % SBS, 15–20 % APP) as compared to the concentrations normally found in modified bitumen for road pavements. As the modifying polymers are not bitumen soluble (thermodynamically miscible), a disperse system is usually formed in which the continuous phase is the bitumen and the dispersed phase is the polymer. By application of intensive mechanical agitation for a period long enough while providing adequate control of the interfacial tension between the bitumen and the polymer, “phase inversion” can occur, i.e. it is obtained an inverse dispersion in which the polymer becomes the continuous phase where bitumen droplets are dispersed [38–40]. Phase inversion is a well-known process in lipid-water systems. Cream (oil dispersed in a continuous water

Table 5.2 North American and European production of bitumen roofing products in 2006 (unit: $km^2 = 10^6\ m^2$)

Waterproofing systems	Cold-applied products		Soft-applied products		Hot-applied products	
	USA	UE	USA	UE	USA	UE
Shingles	3,403	40	0	0	0	0
Bitumen membranes and underlayments	1,418	14	0	256	0	14
Polymer-modified bitumen roofing	235	32	35	514	39	64
BUR (*built-up roofing*)	39	0	0	0	259	2
Total	*5,095*	*86*	*35*	*770*	*298*	*80*
Market share	81 %		13 %		6 %	

Source: The Bitumen Roofing Industry—A Global Perspective (2011) 2nd edition

phase) is transformed into butter (water dispersed in a continuous oil phase) by mechanical agitation.

Built-up waterproofing systems are made of several superimposed layers of fibreglass sheets impregnated with oxidised bitumen or modified bitumen. This type of system is widely used in the United States, but it is not commonly used in Europe [36].

Non-bituminous synthetic membranes are obtained by extrusion or calendering of thermoplastics, e.g. polyvinyl chloride (PVC); thermoplastic elastomers, e.g. ethylene-propylene-diene monomer (EPDM) copolymers; or thermoplastic polyolefins (TPOs). They may or may not be reinforced, and, like bitumen membranes, they are sold in roll form. They are usually applied by cold bonding or by hot air soldering.

Liquid waterproofing systems are based on liquid prepolymers, which subsequently are cured, and a tight polymer network is produced. The most commonly used formulations are composed of:

1. Butyl rubber (poly-isobutylene copolymerised with poly-isoprene) with mineral fillers.
2. Styrene-acrylic dispersions.
3. Polyurethanes.

Utilisation of the different waterproofing systems in 2006 is shown in Table 5.2.

5.4 Bituminous Mixtures

5.4.1 Composition and Properties

In general, a bituminous mixture is a material composed by bitumen binder, aggregates and, eventually, other additives in order to achieve certain special properties or performance useful for the factory process or the performance during the life cycle service.

As described earlier, different bitumen and bituminous binders are available for bituminous mixtures. EN 12591 [S-2] presents the most important specifications for paving grade bitumens. In the composition of the bituminous mixture, it should be always specified: the grade of the bitumen, the type and grade of modified bitumen or the amount and category of natural asphalt. In the case of a paving grade bitumen, the grade shall be selected from the grades between 20/30 and 330/430, inclusively. In the case of a hard grade bitumen, the grade shall be chosen from the grades 10/20 and 15/25.

Aggregates are an important component of the bituminous mixture. It is possible to use in the composition of the bituminous mixtures aggregates and filler aggregates, obtained by processing natural, manufactured or recycled materials. Aggregate sizes in bituminous mixtures are described by the pair d/D corresponding both to sieve sizes in millimetres: d is the lower limit designation sieve and D is the upper limit designation sieve between which most of the particle size distribution lies (e.g. 2/4 mm). It should be noted that this designation accepts the presence of some particles which are retained on the upper sieve (oversize) and some which pass the lower sieve (undersize).

The mixture of aggregates presented in a bituminous mixture is composed by different particle size fractions: fines are the particle size fraction of an aggregate that passes the 0.063 mm sieve; coarse aggregate designation given to the larger aggregate sizes with D greater than 4 mm and d greater than or equal to 1 mm; fine aggregate is the designation given to the smaller aggregate sizes with D less than or equal to 4 mm and $d = 0$. Fine aggregates can be produced from natural disintegration of rock or gravel and/or by the crushing of rock or gravel or processing of manufactured aggregates.

Filler aggregate is the fine aggregate presented in the bituminous mixture, most of which passes a 0.063 mm sieve.

EN 13043 [S-22] (and ASTM D6155 [S-22a], ASTM D692/D692M [S-22b]) specifies the most important properties of aggregates for use in bituminous mixtures and surface treatments of road and airfield pavements. In general, these specifications include geometrical, physical and chemical requirements. In terms of geometrical requirements, it is important to consider the aggregate size, grading, fines content, fines quality and particle shape of coarse and all-in aggregates. Physical requirements needed to the aggregates are related to resistance to fragmentation (Los Angeles), resistance to wear (micro-Deval), particle density and water absorption, bulk density, polishing, resistance to surface abrasion and resistance to abrasion from studded tyres for application in surface courses and affinity to bituminous binder. In some bituminous mixtures it is important to consider some chemical requirements. In addition to a general petrographic description, evaluation of contaminators is important in the case of the use of lightweight coarse aggregate. Volume stability is also important in the case of steel slag. Durability of the aggregates has a special importance for some aggregates: magnesium sulphate soundness of coarse aggregates, freeze-thaw resistance and resistance to thermal shock. Identical requirements should be achieved in the case of filler aggregate, taking into account the same purposes. Table 5.3

Table 5.3 Properties of aggregates and bituminous mixtures (adapted from [33])

Characteristic	Test method
Aggregates	
Assessment of fines	EN 933-9 [S-23]
	ASTM C1777 [S-23a]
Particle shape—Flakiness index	EN 933-3 [S-24]
	ASTM D3398 [S-24a]
Percentage of crushed and broken surfaces in coarse aggregate particles	EN 933-5 [S-25]
	ASTM D5821 [S-25a]
Resistance to fragmentation (Los Angeles)	EN 1097-2 [S-26]
	ASTM C131 [S-26a]
	ASTM C535 [S-26b]
Resistance to wear (micro-Deval)	EN 1097-1 [S-27]
	ASTM D7428 [S-27a]
	ASTM D6928 [S-27b]
Polished stone value[a]	EN 1097-8 [S-28]
	ASTM D3319 [S-28a]
	ASTM E660 [S-28b]
Particle density and water absorption	EN 1097-6 [S-29]
	ASTM C127 [S-29a]
	ASTM C128 [S-29b]
Loose bulk density and voids	EN 1097-3 [S-30]
	ASTM C29/C29M [S-30a]
Resistance to thermal and weathering properties of aggregates	EN 1097-6 [S-29]
	EN 1367-2 [S-31]
Resistance to thermal shock	EN 1367-5 [S-32]
	EN 1097-2 [S-31]
Affinity between aggregate and bitumen	EN 12697-11 [S-33]
	ASTM D5100/D5100M [S-33a]
Sonnenbrand basalt	EN 1367-3 [S-34]
	EN 1097-2 [S-31]
Bituminous mixture	
Marshall characteristics	EN 12697-34 [S-35]
	ASTM D6927 [S-35a]
Voids in mineral aggregates (VMA)	EN 12697-8 [S-36]
	ASTM D3203/D3203M [S-36a]
Voids characteristics	EN 12697-8 [S-36]
	ASTM D3203/D3203M [S-36a]
Ratio filer/binder	–
Resistance	MIL-STD-620A [S-37]
Resistance to permanent deformation ("wheel tracking")	EN 12697-22 [S-38]
Binder content	–

(continued)

Table 5.3 (continued)

Characteristic	Test method
Determination of water sensitivity	EN 12697-12 [S-39]
	ASTM D41075 [S-39a]
	ASTM D4867/D4867M [S-39b]
In situ drainability[b]	EN 12697-40 [S-40]
	ASTM E2380/E2380M [S-40a]
In situ drainability (LCS)[b]	NLT 327 [S-41]
Particle loss[b]	EN 12697-17 [S-42]
Wet Cântabro test[b]	NLT 362 [S-43]

[a] Bituminous mixtures from surface course
[b] Porous asphalt

summarises the main properties of the aggregates required for bituminous mixtures, according the Portuguese experience [33].

Additives are constituent materials which can be added in small quantities. These materials could be inorganic or organic fibres or polymers to influence the mechanical properties, the workability or the colour of the bituminous mixture.

The use of recycled materials in pavements gains a wider acceptance for a more sustainable construction and rehabilitation of the transport infrastructures. An example is the incorporation of steel slag in bituminous mixtures and other recycled aggregates, e.g. crushed concrete from construction and demolition waste. Processed steel slag aggregate is an industrial by-product obtained from the production process of steel and laminates.

The bituminous mixture composition influences the final performance of the material during the life cycle service, taking into account also the climatic and traffic conditions. The most part of mix design methods for bituminous mixtures carried out in Europe and in the United States involves the selection of materials, the study of physical properties of the mixture and the selection of binder content. Other additional parameters are also very important to consider in the bituminous mixture design process, such as workability, coating, water sensitivity, compactability and mechanical performance.

As the bitumen and the bituminous binders, the rheological behaviour of the bituminous mixtures is characterised by the viscosity. So, mechanical performance of bituminous mixtures depends on the loading time and temperature, as the most important parameters [41].

If the composition of bituminous mixtures can be simplified to the presence of aggregates, bitumen and air (three phases), volumetric and gravimetric relationships between the phases can be established. These relationships are important because they allow a better understanding of the bituminous mixtures behaviour. Void and binder contents are some of the most important properties related to the bituminous mixture composition. Void content is mainly influenced by grading and type of aggregate, binder content and the energy and temperature of

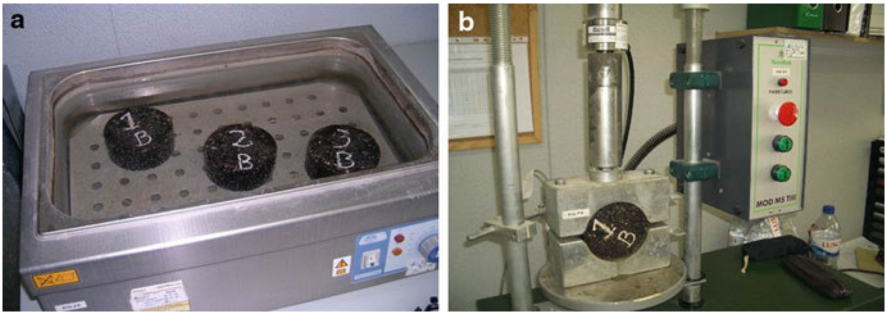

Fig. 5.4 Marshall test: (**a**) specimens immersed in the water bath; (**b**) specimen in the testing machine

compaction. As opposed to dense-graded mixtures with low values of void content (e.g. asphalt concrete), the use of modified bitumen and other additives provides bituminous mixtures characterised by high values of void content—open-graded mixtures—with deformation resistant capacity. This is the case of the porous asphalt [41]. In a continuous-graded mixture with lower void content, a maximum void content is important to limit the permeability and the lack of cohesion, but a minimum of air void is also needed in order to provide the stability in the compacted mixture in terms of bleeding and loss of stability when the bituminous mixture is submitted to climatic and traffic conditions.

The main goal of the bituminous mixture design is to achieve the appropriate quantity of bitumen in order to ensure an adequate coating of the aggregates and to provide a good workability, resistance (stiffness, deformation, fatigue) and durability of the mixture. In the case of surface courses, the bituminous mixtures also should provide for the pavement surface the adequate texture and skid resistance to ensure the passage of vehicles with maximum levels of comfort and safety.

One of the most widely known mix design methods for HMA is based on the Marshall test (EN 12697-34 [S-35]). Different laboratory specimens are compacted in a certain range of bituminous content and are submitted to Marshal test. According the behaviour during the compression test that should fit all the specified requirements for the bituminous mixture, in terms of physical and mechanical characteristics, an optimum binder content is selected. Figure 5.4 shows test specimens at 60 °C inside the water bath (Fig. 5.4a) and a test specimen placed in the compression testing machine (Fig. 5.4b). Other methodologies are available for bituminous mixtures design purposes (e.g. SHRP Superpave).

Typically, bituminous mixtures are composed by aggregate particles continuously graded or gap graded to form an interlocking structure. The European experience considers two ways of specifying the bituminous mixtures: an empirical approach based on compositional recipes and requirements for constituent materials with additional requirements based on performance-related tests and a fundamental approach in terms of performance-based requirements linked to limited prescription of composition and constituent materials.

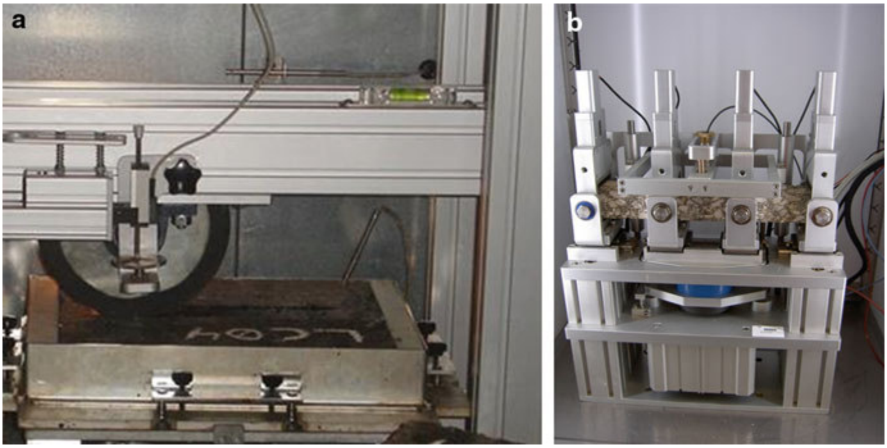

Fig. 5.5 (**a**) Wheel tracking test; (**b**) Resistance to fatigue test

General requirements specified for bituminous mixtures by EN 13108 are composition and grading, void content, coating and homogeneity, water sensitivity, resistance to abrasion by studded tyres, resistance to permanent deformation, reaction to fire, resistance to fuel for application on airfields, resistance to de-icing fluid for application on airfields, temperature of the mixture and durability. The bituminous mixture, when discharged from the mixer, shall be homogenous in appearance and the aggregate shell be also completely coated with the binder. Evidence of balling of fine aggregate shall not be observed in the material. The water sensitivity of the bituminous mixtures shall be tested in accordance with EN 12697-12 [S-39], by the determination of the indirect tensile strength ratio obtained in test specimens. The resistance to permanent deformation is obtained in terms of wheel tracking determined in accordance with EN 12697-22 [S-38]. In Portugal, wheel tracking tests are performed in the small-sized device procedure B conditioning in air (Fig. 5.5a).

The empirical approach includes the material composition (grading, binder content and additives), Marshal values in the case of airfields, voids filled with bitumen and voids in mineral aggregate (VMA). Fundamental requirements are related to composition (grading and binder content), stiffness, resistance to permanent deformation in triaxial compression test and resistance to fatigue [S-44, S-44a] (Fig. 5.5b).

5.4.2 Products and Applications

Depending on the composition and characteristics and the method of production, different bituminous mixtures could be available for road and airfield pavements applications.

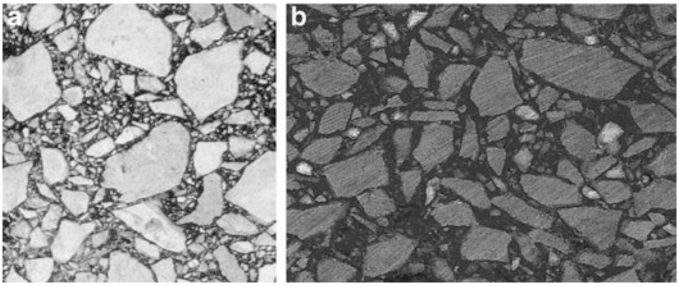

Fig. 5.6 Structure of bituminous mixtures: (**a**) asphalt concrete; (**b**) stone mastic asphalt

In terms of composition and characteristics, taking into account the European experience, the most common bituminous mixtures used in pavements are:

- Asphalt concrete (EN 13108-1) [S-45].
- Asphalt concrete for very thin layers (EN 13108-2) [S-46].
- Soft asphalt (EN 13108-3) [S-47].
- Hot rolled asphalt (EN 13108-4) [S-48].
- Stone mastic asphalt (EN 13108-5) [S-49].
- Mastic asphalt (EN 13108-6) [S-50].
- Porous asphalt (EN 13108-7) [S-51].
- Reclaimed asphalt (EN 13108-8) [S-52].

The asphalt concrete specified in EN 13108-1 [S-45] and EN 13108-2 [S-46] is a dense-graded material with a large scope of application in pavement construction (Fig. 5.6a). The designation of the asphalt concrete is “AC D surf/base/bin binder” where “AC” is asphalt concrete; “D” is the upper sieve size of the mixtures of aggregates; “surf” is the surface course; “base” is the base course; “bin” is the binder course; and “binder” is the designation of binder used. The asphalt concrete “AC 20 base 35/50” is an asphalt concrete with maximum aggregate size 20 mm for base course with penetration bitumen 35/50.

A stone mastic asphalt (SMA) is a gap-graded asphalt concrete mixture with bitumen as a binder, composed of a coarse crushed aggregate skeleton bound with a mastic mortar (Fig. 5.6b). The designation of the stone mastic asphalt is “SMA D binder” where “SMA” is stone mastic asphalt; “D” is the upper sieve size of the mixtures of aggregate; and “binder” is the designation of binder used. The “SMA 11 70/100” is a stone mastic asphalt with maximum aggregate size 11 mm and penetration bitumen 70/100. Due to a high coarse aggregate content that interlocks to form a resistant stone skeleton, SMA provides a high permanent deformation resistance recommended for heavily trafficked roads. In fact, the coarse aggregates provides a more stone-on-stone contact than with conventional dense-graded bituminous mixtures. The presence of fibres in the mastic of bitumen and filler is fundamental in order to provide an adequate stability of the bitumen and to avoid

Fig. 5.7 Texture of the pavement surface in porous asphalt (*left*) and asphalt concrete (*right*)

the drainage of the binder, during the transport and the placement of SMA in pavement construction.

Porous asphalt is a bituminous material with bitumen as a binder prepared so as to have a very high content of interconnected voids which allow passage of water and air in order to provide the compacted mixture with drain and noise reducing characteristics. This type of bituminous mixtures consists of an open-graded coarse aggregate, bonded together by modified bituminous binders. The designation of the porous asphalt is “PA D binder” where “PA” is porous asphalt; “D” is the upper sieve size of the mixtures of aggregates; and “binder” is the designation of binder used. The “PA 11 70/100” is a porous asphalt with maximum aggregate size 11 mm and penetration bitumen 70/100. The surface texture characteristics of porous asphalt provide a higher skid resistance favourable to traffic safety in comparison to the surface characteristics of the bituminous mixture (Fig. 5.7) and also a noise reduction.

Reclaimed asphalt is obtained by milling of asphalt road layers and by crushing of slabs ripped up from asphalt pavements or lumps from asphalt slabs and asphalt from reject and surplus production. Recycling bituminous mixtures results in a reusable mixture of aggregate and asphalt binder known as reclaimed asphalt pavement (RAP). The feedstock of reclaimed asphalt defined the quantity of material to be used as a constituent material for the manufacturing of hot asphalt mixtures. The particle size of reclaimed asphalt is the maximum size of the pieces of asphalt in the reclaimed material, expressed as a sieve size (U). Reclaimed asphalt shall be designated by the abbreviation RA, preceded by the asphalt particle size designation U and followed by the aggregate size designation d/D mm: U RA d/D. The reclaimed asphalt 40 RA 0/8 mm is a reclaimed asphalt, of which the aggregate has an upper sieve size of 8 mm and the asphalt particles have a maximum size of 40 mm.

According the temperature range of production, bituminous mixtures are classified in the following types [42]:

- Cold mixes—produced with unheated aggregate and bitumen emulsion or foamed bitumen.
- Half warm asphalt—produced with heated aggregate at a mixing temperature (of the mix) between approximately 70 °C and roughly 100 °C.
- Warm mix asphalt (WMA)—produced and mixed at temperatures roughly between 100 and 140 °C.
- Hot mix asphalt (HMA)—produced and mixed at temperatures roughly between 120 and 190 °C, depending on the bitumen used.

The most common bituminous mixtures in pavement construction and rehabilitation are HMA that are produced in hot asphalt mixing plants by mixing the aggregates with the bitumen at elevated temperatures. The mixing temperature is sufficiently high in order to obtain the bitumen liquid enough for a proper mixing with and coating the aggregates. However, the temperature should not to be too high as to avoid excessive ageing of the asphalt. A HMA is laid and compacted when it is still sufficiently hot so as to have proper workability. HMA are often used in surface and binder courses in road and airfield pavements.

WMA technologies operate above 100 °C. Various techniques are used to reduce the effective viscosity of the binder enabling full coating and subsequent compactability at lower temperatures [42, 43]. The most common techniques are organic additives, chemical additives and foaming techniques. Organic and chemical additives typically may reduce the mix and compaction temperatures of between 20 and 30 °C. The type of additive must be selected carefully. Advantages and limitations of the use of additives are mentioned in the literature for each process. WMA comprises a great number of bituminous mixtures: asphalt concrete, SMA, porous asphalt, reclaimed asphalt, etc. These bituminous mixtures can be fabricated, laid and compacted by using WMA technologies instead of traditional HMA [43].

WMA has a significant number of advantages comparing to HMA, basically associated with energy saving which lead to a major reduction of emission of greenhouse effect gases, such as carbon dioxide, and pollutants [43].

HMA and WMA are prepared at central mixing plants. In these facilities, aggregates are mixed with the bitumen, eventually additives, to produce the bituminous mixture. Central mixing plants can be portable or stationary (permanent in one location and with greater production capacity). There are two types of central mixing plants: drum mix plants (continuous) and batch plants. Typically, the batch central mixing plant is composed by an area for the aggregates storage (cold feed bins). After the transportation and weighing of the aggregates, the next step is developed in the dryer where the aggregates are blended, heated and dried. In sequence, the hot aggregates are screening, weighing and storing in hot bins, in units mounted at the top of the central mixing plant. Finally, the mix of the aggregates with the bitumen is performed in the mixing unit. The final bituminous mixture is discharged into the trucks used to the transport to the site. In the case of a drum mix plant (Fig. 5.8a), all the process of aggregates heating and mixture with the bitumen is performed in the drum mixer (Fig. 5.8b).

Fig. 5.8 Drum mix plant: (**a**) general view; (**b**) inside part of the drum mixer

Fig. 5.9 Pavement construction: (**a**) asphalt paver; (**b**) rollers operating the bituminous mixture compaction

In the major situations, bituminous mixtures are placed in situ by asphalt pavers that spread the material in a uniform layer with a certain thickness (Fig. 5.9a). Previously, the existing underlying surface should be clean and a prime coat (granular layer) or a tack coat (bituminous layer) is applied. If the surface presents irregularities, an additional levelling is necessary with a bituminous mixture. In the case of thick courses, the bituminous mixtures should be placed in two or more layers. The placement should be performed always with favourable weather conditions (temperature and humidity).

When the spreading and finishing of layers are completed, the compaction is the next phase with the bituminous mixture still hot and workable. The compaction is carried out by pneumatic tyred rollers (asphalt concrete for instance) or steel wheel rollers (porous asphalt, for instance) or by the combination of both types of rollers. In each case, depending on the type of bituminous mixtures, the most adequate method to compaction should be selected (Fig. 5.9b).

The quality control is essential in order to ensure the desirable characteristics of the bituminous mixtures during the construction (e.g. temperature) and after the conclusion of works (e.g. density, void content, roughness, skid resistance and structural resistance).

Fig. 5.10 Alligator cracking in the bituminous mixture of a road pavement

5.4.3 Maintenance, Rehabilitation and Recycling

During life cycle, traffic and weather conditions lead to the degradation of the characteristics of the bituminous materials used in the pavement. The most important distresses are cracking, permanent deformations and disintegration of the aggregates. In the case of bituminous mixtures, the main factors in the origin of these distresses are related to:

- Cracking caused by repeated loading due to the passage of vehicles and associated with the fatigue of the material.
- Cracking due to thermal variations.
- Cracking due to crack propagation from lower courses.
- Cracking from top to bottom due to aggressive loading patterns from traffic.
- Rut depth due to permanent deformation resulting from repeated loading due to the passage of vehicles.
- Disintegrations and loss of aggregates due to the ageing of bitumen.

Figure 5.10 presents a very advanced stage of cracking in the bituminous mixture of a road pavement, designated by “alligator cracking”.

The factors in the origin of the permanent deformations could be the poor compaction of the pavement courses during construction (high voids content) and the low bearing capacity of the pavement foundation or of the granular layers of the pavement, due sometimes to the insufficient conditions of the drainage system.

The disintegrations of the surface layer of the pavement usually result from the ageing of the bitumen and the loss of cohesion of the various components of the bituminous mixture that can also be due to low binder content.

The bituminous mixtures described previously can be used in the maintenance and rehabilitation of pavements. The causes of the distresses observed in the old pavement should be investigated in order to provide the most adequate solution and, consequently, bituminous mixtures. Two main objectives could be considered in the pavement maintenance: the structural reinforcement of the old pavement, in terms of bearing capacity of the pavement and the foundation; the functional maintenance of the pavement surface, in terms of skid resistance, roughness and noise properties.

The surface dressing consists of spraying onto the pavement surface of a thin film of bituminous binder or emulsion followed by the application of single one or more layers of stone chippings. This type of solution is mainly indicated to restore skid resistance, to arrest disintegration or loss of aggregates and to seal pavement cracking and thus protect the pavement structure from damage of water. Epoxy resins and high resistant aggregates, such as calcined bauxite, could be used in resistant surface dressings, sometimes coloured, that are capable of resisting in special conditions of application to the stresses imposed by traffic: roundabouts, approaches to traffic lights, etc. Durability of surface dresses depends on the rate application of the binder; the quality, size and rate of chipping application; and the single or multiple chip and binder applications.

The use of recycled materials in pavements gains a wider acceptance for a more sustainable construction and rehabilitation of the transport infrastructures. An example is the case of reclaimed asphalt that is a material with an enormous potential to be used in new bituminous mixtures.

Recycling of road materials is defined as the reuse of existing materials in the construction and maintenance, with or without changing the characteristics of the material. There are many options for recycling and the choice to be made depends on technical, environmental and economical requirements established for each case. Approaches for recycling are different in various countries based on national needs, requirements, technologies, resources, knowledge, etc.

Guidelines for pavement recycling were established by the World Road Association (PIARC) [44]; several classifications of the main types of bituminous mixtures recycling can be made according to the:

- Place where mixing is carried out.
- Temperature of the process.
- Characteristics of the material to be recycled.
- Type of binder.

According to the place where mixing is carried out, in situ and in plant are possible techniques to use the reclaimed asphalt, with or without adding new materials, to modify or not the characteristics of the materials. If the recycling process to produce a new material is developed in plant, the milled or pulverised bituminous mixture from the old pavement is stockpiled and then processed to obtain an appropriate grading, before the finally mix.

In terms of temperature, the most common processes are cold and hot recycling. Cold recycling consists of milling or crushing the existing materials of the pavement. Then at the same time or in a second operation, it is incorporated in the fragmented pavement material a bituminous binder in the form of emulsion or of foamed bitumen. The objective is to stabilise the recycled course and to give it cohesion. The mixture is compacted to reconstitute the new pavement course. In hot recycling developed in plant, the milled bituminous mixture is hot mixed with bitumen and new aggregates are added for gradation correction if necessary. The reclaimed asphalt is added to virgin material. The resulting mix is placed in road construction as a new asphalt concrete. If hot recycling is performed in situ, special and powerful heating machines are used to elevate the temperature of the pavement and to facilitate the process of milling and mixing.

Each recycling technique has advantages and limits to the use that should be analysed in the process of selection. The development of the recycling technology in the last decades has allowed the increase of this methodology to the rehabilitation of road pavements involving bituminous mixtures.

Standards

[S-1] European Committee for Standardization (CEN)—EN 1426—Bitumen and bituminous binders—Determination of needle penetration. Brussels: CEN (2007)

[S-1a] American Society for Testing and Materials (ASTM)—D5/D5M—Standard Test Method for Penetration of Bituminous Materials. West Conshohocken: ASTM (2013)

[S-2] European Committee for Standardization (CEN)—EN 12591—Bitumen and bituminous binders—Specifications for paving grade bitumens. Brussels: CEN (2009)

[S-3] European Committee for Standardization (CEN)—EN 12597—Petroleum products, bitumen and bituminous binders—Terminology. Brussels: CEN (2000)

[S-3a] American Society for Testing and Materials (ASTM)—D8—Standard Terminology Relating to Materials for Roads and Pavements. West Conshohocken: ASTM (2013)

[S-4] European Committee for Standardization (CEN)—EN 1427—Bitumen and bituminous binders—Determination of the softening point—Ring and ball method. Brussels: CEN (2007)

[S-4a] American Society for Testing and Materials (ASTM)—D36/D36M—Standard Test Method for Softening Point of Bitumen (Ring-and-Ball Apparatus). West Conshohocken: ASTM (2012)

[S-5] European Committee for Standardization (CEN)—EN 13302—Bitumen and bituminous binders—Determination of dynamic viscosity of a bituminous binder using a rotating spindle apparatus. Brussels: CEN (2010)

[S-5a] European Committee for Standardization (CEN)—EN 13302—Bitumen and bituminous binders—Determination of dynamic viscosity of bituminous binder using a rotating spindle apparatus. Brussels: CEN (2010)

[S-6] European Committee for Standardization (CEN)—EN 12607—Bitumen and bituminous binders—Determination of the resistance to hardening under the influence of heat and air- Part 1: RTFOT. Brussels: CEN (2007)

[S-6a] American Society for Testing and Materials (ASTM)—D6521—Standard Practice for Accelerated Aging of Asphalt Binder Using a Pressurized Aging Vessel (PAV). West Conshohocken: ASTM (2013)

[S-7] European Committee for Standardization (CEN)—EN ISO 2592—Petroleum products—Determination of flash and fire points: Cleveland open cup method. Brussels: CEN (2001)

[S-7a] American Society for Testing and Materials (ASTM)—D92—Standard Test Method for Flash and Fire Points by Cleveland Open Cup Tester. West Conshohocken: ASTM (2012)

[S-8] European Committee for Standardization (CEN)—EN 12592—Bitumen and bituminous binders—Determination of solubility. Brussels: CEN (2007)

[S-8a] American Society for Testing and Materials (ASTM)—D5546—Standard Test Method for Solubility of Asphalt Binders in Toluene by Centrifuge. West Conshohocken: ASTM (2009)

[S-8b] American Society for Testing and Materials (ASTM)—D2042—Standard Test Method for Solubility of Asphalt Materials in Trichloroethylene. West Conshohocken: ASTM (2009)

[S-9] European Committee for Standardization (CEN)—EN 12593—Bitumen and bituminous binders—Determination of the Fraass breaking point. Brussels: CEN (2007)

[S-10] European Committee for Standardization (CEN)—EN 12595—Bitumen and bituminous binders—Determination of kinematic viscosity. Brussels: CEN (2007)

[S-10a] American Society for Testing and Materials (ASTM)—D2170/D2170M—Standard Test Method for Kinematic Viscosity of Asphalts (Bitumens). West Conshohocken: ASTM (2010)

[S-11] European Committee for Standardization (CEN)—EN 14023—“Bitumen and bituminous binders—Framework specification for polymer modified bitumens”. Brussels: CEN (2010)

[S-11a] American Society for Testing and Materials (ASTM)—D6154—Standard Specification for Chemically Modified Asphalt Cement for Use in Pavement Construction. West Conshohocken: ASTM (2009)

[S-12] European Committee for Standardization (CEN)—EN 13924—Bitumen and bituminous binders—Specifications for hard paving grade bitumens. Brussels: CEN (2006)

[S-12a] American Society for Testing and Materials (ASTM)—D946/D946M—Standard Specification for Penetration-Graded Asphalt Cement for Use in Pavement Construction. West Conshohocken: ASTM (2009)

[S-13] European Committee for Standardization (CEN)—EN 13808—“Bitumen and bituminous binders, Framework for specifying cationic bituminous emulsions” Brussels: CEN (2005)

[S-13a] American Society for Testing and Materials (ASTM)—D2397—Standard Specification for Cationic Emulsified Asphalt. West Conshohocken: ASTM (2012)

[S-14] European Committee for Standardization (CEN)—EN 13707—Flexible sheets for waterproofing. Reinforced bitumen sheets for roof waterproofing. Definitions and characteristics. Brussels: CEN (2013)

[S-14a] American Society for Testing and Materials (ASTM)—D226/D226M—Standard Specification for Asphalt-Saturated Organic Felt Used in Roofing and Waterproofing. West Conshohocken: ASTM (2009)

[S-14b] American Society for Testing and Materials (ASTM)—D2626/D2626M—Standard Specification for Asphalt-Saturated and Coated Organic Felt Base Sheet Used in Roofing. West Conshohocken: ASTM (2012)

[S-14c] American Society for Testing and Materials (ASTM)—D2178/D2178M—Standard Specification for Asphalt Glass Felt Used in Roofing and Waterproofing. West Conshohocken: ASTM (2013)

[S-15] European Committee for Standardization (CEN)—EN 1109—Flexible sheets for waterproofing—Bitumen sheets for roof waterproofing—Determination of flexibility at low temperature. Brussels: CEN (2013)

[S-16] European Committee for Standardization (CEN)—EN 1110—Flexible sheets for waterproofing. Bitumen sheets for roof waterproofing. Determination of flow resistance at elevated temperature. Brussels: CEN (2010)

[S-17] European Committee for Standardization (CEN)—EN 1296—Flexible sheets for waterproofing—Bitumen, plastic and rubber sheets for roofing—Method of artificial ageing by long term exposure to elevated temperature. Brussels: CEN (2001)

[S-18] European Committee for Standardization (CEN)—EN 1297—Flexible sheets for waterproofing—Bitumen, plastic and rubber sheets for roofing—Method of artificial ageing by long term exposure to the combination of UV radiation, elevated temperature and water. Brussels: CEN (2004)

[S-19] European Committee for Standardization (CEN)—EN 12594—Bitumen and bituminous binders. Preparation of test samples. Brussels: CEN (2004)

[S-19a] American Society for Testing and Materials (ASTM)—D140/D140M—Standard Practice for Sampling Bituminous Materials. West Conshohocken: ASTM (2009)

[S-20] American Society for Testing and Materials (ASTM)—D449-03—Standards specification for asphalt used in dampproofing and waterproofing. West Conshohocken: ASTM (2008)

[S-21] Associación Española de Normalización y Certificación (AENOR)—Reglamento particular de la marca AENOR para impermeabilizantes bituminosos para cubiertas. Madrid: AENOR, (2010)

[S-22] European Committee for Standardization (CEN)—EN 13043 Aggregates for bituminous mixtures and surface treatments for roads, airfields and other trafficked areas. Brussels: CEN (2002)

[S-22a] American Society for Testing and Materials (ASTM)—D6155—Standard Specification for Nontraditional Coarse Aggregates for Bituminous Paving Mixtures. West Conshohocken: ASTM (2013).

[S-22b] American Society for Testing and Materials (ASTM)—D692/D692M—Standard Specification for Coarse Aggregate for Bituminous Paving Mixtures. West Conshohocken: ASTM (2009).

[S-23] European Committee for Standardization (CEN)—EN 933-9—Tests for geometrical properties of aggregates. Part 9: Assessment of fines—Methylene blue test. Brussels: CEN (2009)

[S-23a] American Society for Testing and Materials (ASTM)—C1777—Standard Test Method for Rapid Determination of the Methylene Blue Value for Fine Aggregate or Mineral Filler Using a Colorimeter. West Conshohocken: ASTM (2013)

[S-24] European Committee for Standardization (CEN)—EN 933-3 Tests for geometrical properties of aggregates. Part 3: Determination of particle shape — Flakiness index. Brussels: CEN (2013)

[S-24a] American Society for Testing and Materials (ASTM)—D3398—Standard Test Method for Index of Aggregate Particle Shape and Texture. West Conshohocken: ASTM (2006)

[S-25] European Committee for Standardization (CEN)—EN 933-5/A1 Tests for geometrical properties of aggregates—Part 5: Determination of percentage of crushed and broken surfaces in coarse aggregate particles. Brussels: CEN (2013)

[S-25a] American Society for Testing and Materials (ASTM)—D5821—Standard Test Method for Determining the Percentage of Fractured Particles in Coarse Aggregate. West Conshohocken: ASTM (2006)

[S-26] European Committee for Standardization (CEN)—EN 1097-2—Tests for mechanical and physical properties of aggregates. Part 2: Methods for the determination of resistance to fragmentation. Brussels: CEN (2010)

[S-26a] American Society for Testing and Materials (ASTM)—C131—Standard Test Method for Resistance to Degradation of Small-Size Coarse Aggregate by Abrasion and Impact in the Los Angeles Machine. West Conshohocken: ASTM (2006)

[S-26b] American Society for Testing and Materials (ASTM)—C535—Standard Test Method for Resistance to Degradation of Large-Size Coarse Aggregate by Abrasion and Impact in the Los Angeles Machine. West Conshohocken: ASTM (2012)

[S-27] European Committee for Standardization (CEN)—EN 1097-1 Tests for mechanical and physical properties of aggregates. Part 1: Determination of the resistance to wear (micro-Deval). Brussels: CEN (2011)

[S-27a] American Society for Testing and Materials (ASTM)—D7428—Standard Test Method for Resistance of Fine Aggregate to Degradation by Abrasion in the Micro-Deval Apparatus. West Conshohocken: ASTM (2008)

[S-27b] American Society for Testing and Materials (ASTM)—D6928—Standard Test Method for Resistance of Coarse Aggregate to Degradation by Abrasion in the Micro-Deval Apparatus. West Conshohocken: ASTM (2010)

[S-28] European Committee for Standardization (CEN)—EN 1097-8—Tests for mechanical and physical properties of aggregates. Determination of the polished stone value. Brussels: CEN (2009)

[S-28a] American Society for Testing and Materials (ASTM)—D3319—Standard Practice for Accelerated Polishing of Aggregates Using the British Wheel. West Conshohocken: ASTM (2011).

[S-28b] American Society for Testing and Materials (ASTM)—E660-90—Standard Practice for Accelerated Polishing of Aggregates or Pavement Surfaces Using a Small-Wheel, Circular Track Polishing Machine. West Conshohocken: ASTM (2011).

[S-29] European Committee for Standardization (CEN)—EN 1097-6—Tests for mechanical and physical properties of aggregates. Part 6: Determination of particle density and water absorption. Brussels: CEN (2013)

[S-29a] American Society for Testing and Materials (ASTM)—C127—Standard Test Method for Density, Relative Density (Specific Gravity), and Absorption of Coarse Aggregate. West Conshohocken: ASTM (2012)

[S-29b] American Society for Testing and Materials (ASTM)—C128—Standard Test Method for Density, Relative Density (Specific Gravity), and Absorption of Fine Aggregate. West Conshohocken: ASTM (2012)

[S-30] European Committee for Standardization (CEN)—EN 1097-3—Tests for mechanical and physical properties of aggregates. Determination of loose bulk density and voids. Brussels: CEN (1998)

[S-30a] American Society for Testing and Materials (ASTM)—C29/C29M—Standard Test Method for Bulk Density ("Unit Weight") and Voids in Aggregate. West Conshohocken: ASTM (2009)

[S-31] European Committee for Standardization (CEN)—EN 1367-2—Tests for thermal and weathering properties of aggregates. Part 2: Magnesium sulfate test. Brussels: CEN (2009)

[S-32] European Committee for Standardization (CEN)—EN 1367-5—Tests for thermal and weathering properties of aggregates. Determination of resistance to thermal shock. Brussels: CEN (2011)

[S-33] European Committee for Standardization (CEN)—EN 12697-11—Bituminous mixtures. Test methods for hot mix asphalt. Part 11: Determination of the affinity between aggregate and bitumen. Brussels: CEN (2005)

[S-33a] American Society for Testing and Materials (ASTM)—D5100/D5100M—Standard Test Method for Adhesion of Mineral Aggregate to Hot Bitumen. West Conshohocken: ASTM (2010)

[S-34] European Committee for Standardization (CEN)—EN 1367-3—Tests for thermal and weathering properties of aggregates. Boiling test for Sonnenbrand basalt. Brussels: CEN (2009)

[S-35] European Committee for Standardization (CEN)—EN 12697-34—Bituminous mixtures. Test methods for hot mix asphalt. Marshall test. Brussels: CEN (2012)

[S-35a] American Society for Testing and Materials (ASTM)—D6927—Standard test method for Marshall Stability and Flow of Bituminous Mixtures. West Conshohocken: ASTM (2006)

[S-36] European Committee for Standardization (CEN)—EN 12697-8—Bituminous mixtures. Test methods for hot mix asphalt. Part 8: Determination of void characteristics of bituminous specimens. Brussels: CEN (2003)

[S-36a] American Society for Testing and Materials (ASTM)—D3203/ D3203M—Standard Test Method for Percent Air Voids in Compacted Dense and Open Bituminous Paving Mixtures. West Conshohocken: ASTM (2011)

[S-37] US Army, MIL-STD-620A—Military Standard: Test methods for bituminous paving materials (1966)

[S-38] European Committee for Standardization (CEN)—EN 12697-22—Bituminous mixtures. Test methods for hot mix asphalt. Part 22: Wheel tracking. Brussels: CEN (2009)

[S-39] European Committee for Standardization (CEN)—EN 12697-12—Bituminous mixtures. Test methods for hot mix asphalt. Part 12: Determination of the water sensitivity of bituminous specimens. Brussels: CEN (2008)

[S-39a] American Society for Testing and Materials (ASTM)—D41075—Standard Test Method for Effect of Water on Compressive Strength of Compacted Bituminous Mixtures. West Conshohocken: ASTM (2011)

[S-39b] American Society for Testing and Materials (ASTM)—D4867/ D4867M—Standard Test Method for Effect of Moisture on Asphalt Concrete Paving Mixtures. West Conshohocken: ASTM (2009)

[S-40] European Committee for Standardization (CEN)—EN 12697-40—Bituminous mixtures. Test methods for hot mix asphalt. Part 40: In situ drainability. Brussels: CEN (2005)

[S-40a] American Society for Testing and Materials (ASTM)—E2380/ E2380M—Standard Test Method for Measuring Pavement Texture Drainage Using an Outflow Meter. West Conshohocken: ASTM (2009)

[S-41] NLT 327—Permeabilidad in situ de pavimentos drenantes com el permeámetro LCS (2000)

[S-42] European Committee for Standardization (CEN)—EN 12697-17 + A1—Bituminous mixtures—Test methods for hot mix asphalt—Part 17: Particle loss of porous asphalt specimen. Brussels: CEN (2007)

[S-43] NLT 362—Efecto del agua sobre la cohesión de mezclas betuminosas de granulometría abierta, mediante el ensayo cántabro de pérdida por desgaste (1992)

[S-44] European Committee for Standardization (CEN)—EN 12697-24—Bituminous mixtures. Test methods for hot mix asphalt. Part 24: Resistance to fatigue. Brussels: CEN (2007)

[S-44a] American Society for Testing and Materials (ASTM)—D7460—Standard Test Method for Determining Fatigue Failure of Compacted Asphalt Concrete Subjected to Repeated Flexural Bending. West Conshohocken: ASTM (2010).

[S-45] European Committee for Standardization (CEN)—EN 13108-1—Bituminous mixtures—Material specifications—Part 1: Asphalt Concrete. Brussels: CEN (2008)

[S-46] European Committee for Standardization (CEN)—EN 13108-2—Bituminous mixtures—Material specifications—Part 2: Asphalt Concrete for very thin layers. Brussels: CEN (2006)

[S-47] European Committee for Standardization (CEN)—EN 13108-3—Bituminous mixtures—Material specifications—Part 3: Soft Asphalt. Brussels: CEN (2006)

[S-48] European Committee for Standardization (CEN)—EN 13108-4—Bituminous mixtures—Material specifications—Part 4: Hot Rolled Asphalt. Brussels: CEN (2006)

[S-49] European Committee for Standardization (CEN)—EN 13108-5—Bituminous mixtures—Material specifications—Part 5: Stone Mastic Asphalt. Brussels: CEN (2006)

[S-50] European Committee for Standardization (CEN)—EN 13108-6—Bituminous mixtures—Material specifications—Part 6: Mastic Asphalt. Brussels: CEN (2006)

[S-51] European Committee for Standardization (CEN)—EN 13108-7—Bituminous mixtures—Material specifications—Part 7: Porous Asphalt. Brussels: CEN (2006)

[S-52] European Committee for Standardization (CEN)—EN 13108-8—Bituminous mixtures—Material specifications—Part 8: Reclaimed asphalt. Brussels: CEN (2005)

Books/Magazines/Journals

International Journal of Pavement Engineering
Road Materials and Pavement Design
Construction and Building Materials
Materials and Structures

Associations/Organisations/Societies

- EAPA—European Asphalt Pavement Association: http://www.eapa.org/
- PIARC—World Road Association: http://www.piarc.org/
- ISAP—International Society for Asphalt Pavements: http://asphalt.org/
- AAPT—Association of Asphalt Paving Technologists: http://www.asphalttechnology.org/

Companies

- Shell Company: http://www.shell.com/
- BP: http://www.bp.com/
- CEPSA: http://www.cepsa.com/
- GALP: http://www.galpenergia.com/

References

1. Boëda E et al (1996) Bitumen as a hafting material on Middle Palaeolithic artefacts. Nature 380:336–38
2. Connan J (1999) Use and trade of bitumen in antiquity and prehistory: molecular archaeology reveals secrets of past civilizations. Philos Trans R Soc Lond B Biol Sci 354:33–50
3. Read J, Whiteoak D (2003) (Shell Bitumen)—the Shell Bitumen handbook, 5th edn. Thomas Telford Publishing, Tonbridge
4. Corbett LW (1969) Composition of asphalt based on generic fractionation, using solvent deasphaltening, elution-adsorption chromatography, and densimetric characterization. Anal Chem 41:576–79
5. Brooks C (1991) Initial results from thin layer chromatography in asphalt research. NRCA—3rd International Symposium on Roofing Technology, Gaithersburg, Maryland, USA, 99–105
6. Ecker A (2001) The application of iatroscan-technique for analysis of bitumen. Petrol Coal 43:51–53
7. Masson J-F et al (2001) Dynamics of bitumen fractions by thin-layer chromatography/flame ionization detection. Energy Fuel 15:955–60
8. Fuhr BJ et al (2005) Comparison of bitumen fractionation methods. Energy Fuel 19:1327–29
9. Merdrignac I, Espinosa D (2007) Physicochemical characterization of petroleum fractions: the state of the art. Oil Gas Sci Tech 62:7–32
10. Wang S et al (2010) The development of a method for the qualitative and quantitative determination of petroleum hydrocarbon components using thin-layer chromatography with flame ionization detection. J Chromatogr A 1217:368–74
11. Groenzin H, Mullins O (2001) Molecular size and structure of asphaltenes. Petrol Sci Tech 19:219–30
12. Lu X et al (2005) Wax morphology in bitumen. J Mater Sci 40:1893–1900
13. Pereira JC et al (2007) Resins: the molecules responsible for the stability/instability phenomena of asphaltenes. Energy Fuel 21:1317–1321
14. Nellensteyn FI (1938) The colloidal structure of bitumen. Science of petroleum, vol 4. Oxford University Press, London
15. Pfeiffer JP, Saal RNJ (1940) Asphaltic bitumen as colloid system. J Am Chem Soc 44:139–149
16. Dickie JP, Yen TF (1967) Macrostructures of the asphaltic fractions by various instrumental methods. Anal Chem 39:1847–52
17. Rostler FS, White RM (1959). Influence of chemical composition of asphalts on performance, particularly durability. ASTM Spec. Tech. Pub No. 227
18. Löber L et al (1998) Bitumen in colloid science: a chemical, structural and rheological approach. Fuel 77:1443–50
19. Bonemazzi F, Giavarini C (1999) Shifting the bitumen from sol to gel. J Petrol Sci 22:17–24
20. Lesueur D (2009) The colloidal structure of bitumen: consequences on the rheology and on the mechanisms of bitumen modification. Adv Colloid Interface Sci 145:42–82
21. Löber L et al (1996) New direct observations of asphalts and asphalt binders by scanning electron microscopy and atomic force microscopy. J Microsc 182:32–39
22. Jäger A et al (2004) Identification of microstructural components of bitumen by means of atomic force microscopy (AFM). Proc Appl Math Mech 4:400–1
23. Masson J-F et al (2006) Bitumen morphologies by phase-detection atomic force microscopy. J Microsc 221:17–29
24. Costa ER et al (2008) Bitumen morphology as observed by phase-detection atomic force microscopy. Mater Sci Forum 587–588:981–85
25. Barbosa T et al (1998) Rheological characterization of asphalt bitumens modified with reactive polyurethanes. Les Cahiers de Rhéologie 16(1):527–32
26. Navarro FJ et al (2006) Rheology and microstructure of MDI-PEG reactive prepolymer-modified bitumen. Mech Time-Depend Mat 10:347–59

27. Martín-Alfonso MJ et al (2009) Effect of processing temperature on the bitumen/MDI-PEG reactivity. Fuel Process Tech 90:525–30
28. Lu X, Isacsson U (2002) Effect of ageing on bitumen chemistry and rheology. Construct Build Mater 16:15–22
29. Sá da Costa M et al (2010) Chemical and thermal characterization of road bitumen aging. Mater Sci Forum 636–637:273–79
30. PIARC (1999) Use of modified binders, binders with additives and special bitumens in road pavements. World Road Association, Routes and Roads, no. 303, pp 9–179
31. Aglan H, Lewandowski L, Little D (1996) Polymer modifiers for improved performance of asphalt mixtures. Basel, Technomic AG
32. Navarro FJ et al (2009) Bitumen modification with reactive and non-reactive (virgin and recycled) polymers: a comparative analysis. J Ind Eng Chem 15:458–464
33. Technical Specifications. Pavements. Estradas de Portugal. Portuguese Road Administration, Portugal (2009) (in Portuguese)
34. APORBET (1998) Misturas betuminosas. Contribuição para a normalização do fabrico e da aplicação. Associação Portuguesa de Fabricantes de Misturas Betuminosas (in Portuguese)
35. Asphalt Institute and Eurobitume (2008) The bitumen industry—a global perspective. Production, chemistry, use, specification and occupational exposure, 1st edn. Asphalt Institute and Eurobitume, Lexington
36. Bitumen Waterproofing Association (BWA), et al (2008) The Bitumen Roofing Industry—a global perspective. Production, use, properties, specifications and occupational exposure. ARMA, BWA, NRCA and RCMA
37. Pacheco AC (2010) Qualificação de betumes para a produção de membranas de impermeabilização, Dissertação de Mestrado, Instituto Superior Técnico, Universidade Técnica de Lisboa
38. Union Europeenne pour l'Agrément Technique dans la Construction (UEAtc) (2001) Technical guide for the assessment of Roof Waterproofing Systems made of reinforced APP or SBS polymer modified bitumen sheets. UEAtc, Paris
39. Sengoz B, Isikyakar G (2008) Analysis of styrene-butadiene-styrene polymer modified bitumen using fluorescent microscopy and conventional test methods. J Hazard Mater 150:424–432
40. Sengoz B, Isikyakar G (2008) Evaluation of the properties and microstructure of SBS and EVA polymer modified bitumen. Construct Build Mater 22:1897–1905
41. Branco F, Pereira P, Picado Santos L (2005) Pavimentos Rodoviários, Edições Almedina, Coimbra, Portugal (in Portuguese)
42. EAPA (2010) Position paper—the use of warm mix asphalt. European Asphalt Pavement Association, Brussels
43. Capitão SD, Picado-Santos LG, Martinho F (2012) Pavement engineering materials: review on the use of warm-mix asphalt. Construct Build Mater 36:1016–1024, http://dx.doi.org/10.1016/j.conbuildmat.2012.06.038. doi:10.1016/j.conbuildmat.2012.06.038
44. PIARC (2003) Pavement recycling. PIARC Committee C7/8—"Road Pavements", France, ISBN: 2-84060-154-0

Steel for Civil Construction

6

Rogério Colaço

Abstract

Steel began to be used intensively in civil construction in the first quarter of the nineteenth century. By the end of this century, steel was commonly used as reinforcing material in concrete structures, increasing resistance to levels that the fragile Portland cement could not support by itself. The use of steel as a structural material in civil construction led to a deep change in the limits of the project. For a layperson, the major difference between constructions of the twentieth century and the constructions dating from any other time is their volume. The former are larger and taller, with longer arches and spans. This radical change is a consequence of steel's introduction into construction and of its unique properties. In this chapter we will try to briefly describe the main characteristics of this material, particularly the ones that are important when we think of steels as civil construction materials.

Keywords

Steel • Phase diagram • Ferrite • Cementite • Austenite • Perlite • Martensite • Quenching • Tempering • Annealing • Yield stress • Young's modulus • Resilience • Toughness • Rupture • Welding

6.1 Introduction

Steel began to be used intensively in civil construction in the first quarter of the nineteenth century as the natural consequence of two events: at one hand, the development of technology that enables for the industrial production of large

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M.C. Gonçalves, F. Margarido (eds.), *Materials for Construction and Civil Engineering*, DOI 10.1007/978-3-319-08236-3_6

quantities of steel in an economically feasible way; at the other, the need to build extensive railway lines that used large quantities of steel components with standardised shapes and sizes. These two events lead to the development of engineering solutions, so that standard steel components could be mass produced in large scales. The use of steel as a structural material in civil construction gave rise to a new building paradigm, which took advantage of the possibility of building structures in blocks, using the preformed mass-produced steel. By the end of the nineteenth century, steel would also be used as a reinforcing material in concrete structures (in the form of beams, bars or mesh), increasing resistance to tensile forces to levels that the fragile Portland cement could not support by itself.

Steels have a huge range of mechanical properties, high tensile and compressive strength, stiffness and toughness and can be enformed by plastic deformation. They also have good weldability and the capacity to absorb energy without breaking. All these factors allow for wider selection and adaptation to use, increasing the designer’s freedom when designing the project. The introduction of this material into civil construction led to a deep change in project limits and, therefore, buildings’ limits in terms of volume and space. For a layperson, the major difference between large-scale constructions from the twentieth century and the constructions dating from any other time is their volume. The former are larger, taller, and have longer arches and spans. This radical change in buildings’ volume is a consequence of steel’s introduction into construction.

On the other hand, the use of steel in civil construction provided a flexibility in the shapes and sizes of structures that had not existed before that point, producing a new paradigm in architectural construction: designing a building or structure not as a form but as a process.

Before beginning this chapter, it is important to note that the term “steel” does not refer to one material in particular. Moreover, it refers to a range of materials (several hundred of different metallic alloys are known as “steel”) that are extraordinarily diverse in terms of their chemical composition, microstructure, properties and, of course, possible uses. All the different materials known as “steel” have in common the fact that their main component is iron, i.e. steel is an iron-based metal alloy.

This chapter will try to briefly describe the main characteristics of these alloys, particularly the types of steel that have the greatest number of possible uses in civil construction, but we will begin by the secret of steels: the crystalline allotropic forms of iron and the extraordinary complexity of the Fe-rich region of the Fe-C phase diagram.

6.2 The Crystal Structure of Iron

A range of factors seem to come together to explain the unbeatable success of steel (s) as an engineering material. The first of these factors is certainly the fact that iron, the main component of every steel, is found in extraordinary abundance in the

Earth's crust and, consequently, its alloys are (or can be) cheap compared with other metal alloys based on less abundant elements (titanium, cobalt, nickel, etc.).

Iron is a transition metal and is solid at room temperature. This means that in a piece of iron, the atoms are bound by a strong chemical bond, known as metallic bonding. This type of bond, which is common to all compounds known as metals and which we easily recognise (for their shine, sense of cold to the touch, ductility, etc.), has the particularity of all its atoms sharing their outermost electrons with each other, forming a band of free electrons (valence band) that maintains the cohesion of the whole. The existence of this band of free electrons (free in the sense that they can move freely, since they do not belong to any one atom in particular) is responsible for one peculiarity exclusive to metals: the fact that they conduct electricity.

However, iron appears in nature bonded to oxygen, that is, in the form of iron oxides: hematite (Fe_2O_3) or magnetite (Fe_3O_4). In terms of properties, these iron ores have little or nothing in common with pure iron and even less with steel. To obtain steel, the oxygen must be taken out of the ore, which is known as reducing iron oxide to produce metallic iron. It is not known how iron oxide was reduced for the first time, but it is known that there is a greater affinity between carbon and oxygen than iron and oxygen. Therefore oxygen tends to move from iron to carbon if the temperature is high enough for a reaction to take place. It is therefore assumed (or rather speculated) that metallic iron was obtained for the first time when fires were made in sands rich in iron ore, using wood or coal as fuel: the carbon in the wood or coal would have taken the oxygen from the iron and a ductile material, with a grey sheen, that stood lying in the ashes would have attracted our ancestors' attention. That material was metallic iron or steel because carbon was within it. In fact, by heating the iron ore in the fire, the oxide would have been reduced, but some carbon would have entered the iron as well. It is this combination of iron and carbon, which first took place thousands of years ago, that produced steel for the first time. Point 4 of this chapter explains the effects of carbon on the mechanical properties of steels in more detail.

Metallic bonding keeps the iron atoms arranged in an organised shape. This organisation of iron atoms is known as a crystal structure. The iron atoms are arranged according to a cubic shape. Line after line, row after row, the cubes form a plane, and plane after plane, the entire space is filled by these cubes. If we took one of the cubes at room temperature, we would see eight iron atoms occupying the corners of the cube, and one in the centre. Materials scientists call this organised arrangement of iron atoms a body-centred cubic (BCC) structure. We therefore find that solid iron atoms at room temperature form a crystal with a body-centred cubic structure (Fig. 6.1a). This type of iron—this phase—is known as ferrite and it may contain other types of atoms dissolved in it as we will see later on.

Iron melts at 1539 °C. However, between room temperature and 1539 °C, other transformations occur before melting. At 912 °C, the shape of the organisation of iron atoms changes: eight iron atoms continue to occupy the corners of the cube, but the central atom disappears and six new atoms are found in the centre of each face of the cube instead. In other words, at temperatures higher than 912 °C, iron's

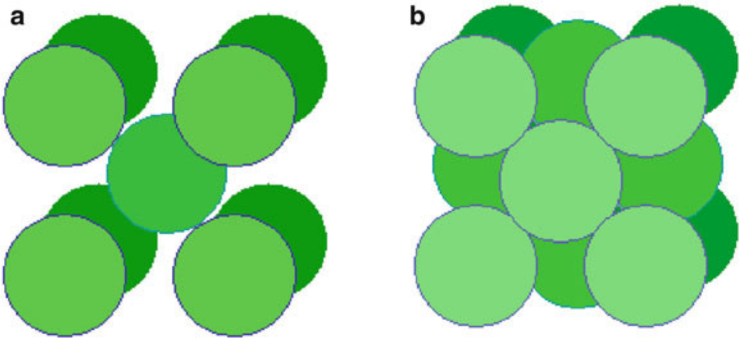


Fig. 6.1 (**a**) Body-centred cubic crystal structure ($T_{room} < T < 912$ °C); (**b**) face-centred cubic crystal structure (912 °C $< T <$ 1,394 °C)

crystal structure changes: it stops being a body-centred cubic structure and instead becomes a face-centred cubic (FCC) structure (Fig. 6.1b). This phase is called austenite and is a phase with greater compactness than ferrite. For this reason, the ferrite → austenite transformation during heating means the iron shrinks on heating, which can have some significant technological implications (accumulation of internal stresses, distortions, cracking).

As the temperature increases, the iron atoms rearrange themselves once again before melting happens. At 1394 °C, they regroup themselves once again in the BCC crystal structure. These changes in iron's crystal structure during heating until melting are known as allotropic transformations and have dramatic implications for steels' properties.

6.3 Mechanical Properties

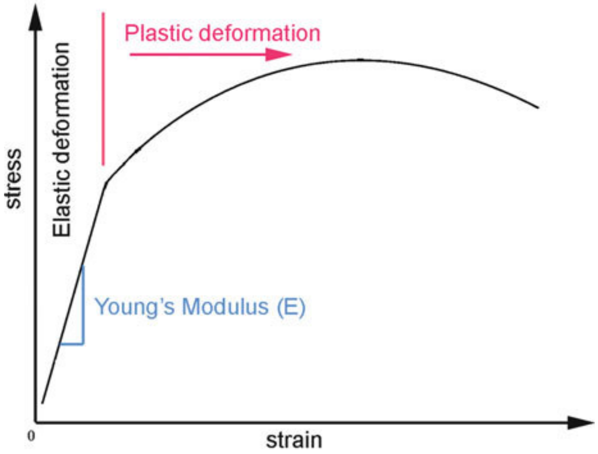
Generally speaking, construction steels (and metallic alloys) are ductile, i.e. they can undergo considerable plastic deformation before fracture. At this point we will consider some specific aspects related to this type of behaviour.

A stress–strain (or force-elongation) curve obtained from a uniaxial tensile test for a steel typically looks like that shown in Fig. 6.2. This curve shows a range of characteristics and establishes a set of parameters that are fundamental to characterising steels' mechanical properties, which we will discuss later.

6.3.1 Elastic Deformation

The first section of the curve, whereas the stress varies in a direct proportion of the strain variation, corresponds to the material's elastic deformation. The elastic deformation regime is characterised by total reversibility, i.e. after the load is removed, the material recovers its original shape. The gradient of this curve is the

Fig. 6.2 Typical uniaxial tensile curve for a metallic material



Young's modulus, E, and has a value that is approximately constant for all steels: around 200 GPa. The value of E is a measure of a material's stiffness: a material with a higher Young's modulus will deform less in the elastic regime when subjected to a certain stress.

The area below the stress–strain curve has units of energy per unit of volume. The area below the stress–strain curve in the elastic section is the energy that the material can absorb reversibly, and is known as resilience. The maximum stress that the material can undergo in the elastic regime is known as yield strength, σ_{yield}. The yield strength is a vitally important parameter for the project designer, seeing as, when in service, the material must never undergo stress levels higher than this value. This would involve permanent deformation of the component (or a break, if the material is brittle).

For most materials, there is no discontinuity in the stress–strain curve's derivative (as there is in Fig. 6.2), which makes it more difficult to determine the exact yield strength. In these cases, some (more or less arbitrary) criteria are used to determine yield strength. One of the most commonly used criteria is the so-called offset yield point at 0.2 %, where a line is drawn parallel to the tensile curve starting at 0.2 % to determine the point where it intersects with the tensile curve (Fig. 6.3a). The intersection point is the yield point at 0.2 %. This stress naturally corresponds to an estimated yield strength, which will need to be compensated for in the project with an appropriate safety factor.

In mild annealed steels (typically steels with a carbon content of less than 0.05 %), the yield point is discontinuous, i.e. there is a plateau in the transition from the elastic deformation regime to the plastic deformation regime, as shown in Fig. 6.3b.

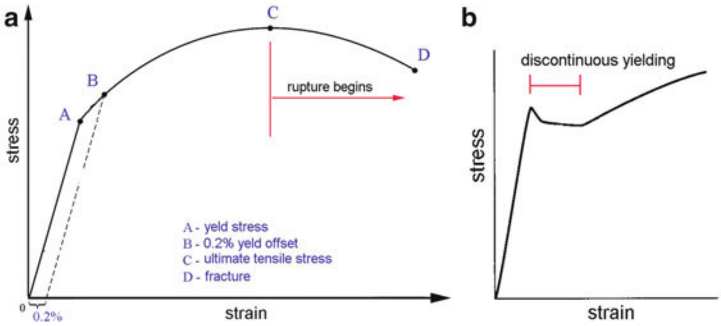


Fig. 6.3 (**a**) Determination of the offset yield point at 0.2 %; (**b**) discontinuous yield point in a mild carbon steel; (**c**) load-unload cycle in which the yield strength is exceeded

6.3.2 Plastic Deformation

Once yield strength has been exceeded, the material enters the plastic deformation regime, i.e. a regime in which deformation is permanent. The section of the tensile curve corresponding to plastic deformation is characterised by a non-linear variation of stress and strain, which makes it possible to easily differentiate the two deformation regimes. In a uniaxial tensile test, if yield strength is exceeded, only the elastic deformation component is recovered, the material is unloaded (Fig. 6.3c), and there may be an increase in the length of the sample and a permanent reduction in the area perpendicular to the tensile axis.

In spite of this non-linear variation, for metal alloys at room temperature, an increase in plastic deformation generally involves an increase in the stress applied. Therefore variation in stress with the strain of the metal alloys in the plastic regime can be approximated by a power law, such as

$$\text{Stress} = \text{K}(\text{strain})^{\text{n}}$$

in which K and n are the material's characteristic constants. The continuous increase in stress necessary for the material to continue being deformed plastically is known as work hardening. Work hardening will be discussed again in point 6, particularly the way in which we can take advantage of this characteristic to increase steel's mechanical strength*.

The load vs. elongation or nominal stress vs. nominal strain curve (see definitions, for example, in G. E. Dieter, *Mechanical Metallurgy*, 3rd edition, McGraw-Hill Book Company, 1988) of a metal subjected to a uniaxial tensile force has its maximum point in the plastic deformation regime (Fig 6.4). This maximum point represents the start of the rupture process, which leads to the material fracture. Until that maximum point is reached, plastic deformation of the specimen is uniform and is therefore known as the stress corresponding to maximum uniform stress (σ_{mu}).

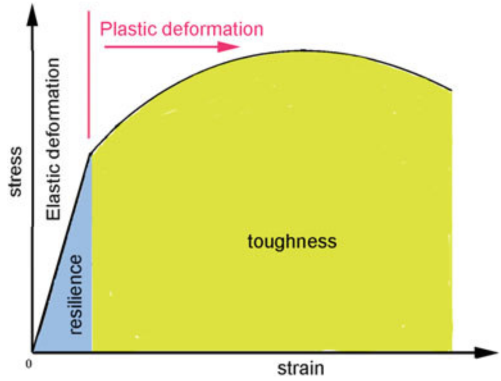


Fig. 6.4 Summary of the main parameters for mechanical characterisation that can be taken from a uniaxial tensile curve

Once the σ_{mu} value has been exceeded, microcracks begin to appear inside the material, and those microcracks propagate and deformation stops being uniform: the speed of deformation in the area where the cracks appear is greater than the speed of deformation in other parts of the specimen, due to the concentration of strain around the cracks, thus producing localised deformation. The area of localised deformation in a uniaxial tensile test is known as the necking and it is where the fracture of the material takes place. The value of the maximum uniform stress imposes a limit on the maximum plastic deformation to which the material can be subjected before being put into service. As an example, let us imagine a steel panel is subjected to bending and later placed in a certain structural use. If during bending σ_{mu} has been exceeded in a specific part of the panel, then the rupture process has begun in that region and small microcracks have formed inside the material. Although the microcracks may not be detectable through observation (whether macroscopic or microscopic), they are points where stresses are concentrated, and may propagate gradually when the panel is placed in service, even if it is subjected to stresses lower than the yield stresses shown in the table. This may lead, therefore, to an extemporaneous fracture in the component, which is difficult to foresee during the planning stage.

The area below the tensile curve is the energy (per unit of volume) absorbed by the material from the start of deformation until fracture. This is known as toughness. The following point will discuss some particularities of this important mechanical characteristic of a material.

6.3.3 Toughness, Ductile Fracture and Brittle Fracture

As mentioned before, toughness is the energy that the material absorbs (or dissipates) through plastic deformation until fracture. Toughness, in general, is not directly considered in the construction project. Nonetheless, it is an important property, above all in choosing structural steels that will be used in conditions that may result in risk of a brittle fracture (brittle fracture is understood in this context to be a fracture that occurs with a minimum of plastic deformation in the material).

A material's toughness may be estimated, above all, in two ways:

- *By the area below the tensile curve* (as mentioned previously). This method is not adequate because it is not very representative of the material's response under sudden impact conditions, i.e. a steel that shows a relatively high toughness for low deformation speeds may have brittle behaviour if the impact velocity is high.
- *By using standardised impact tests* (Charpy or Izod tests). In these tests, a moving pendulum is made to collide with a specimen of a standard shape and size, and the energy dissipated in the fracture is measured.

In practice, impact tests are the most commonly used method for determining a material's toughness, and these tests are particularly used to determine the ductile–brittle transition temperature of the material ($TT_{\text{ductile/brittle}}$). The ductile–brittle transition is a transition found in some steels where the mechanical behaviour of the material stops being essentially ductile and becomes brittle instead, when the temperature is lower than a certain critical value (the $TT_{\text{ductile/brittle}}$). It should be considered with some care when choosing materials, especially if the structure will be subjected to environmental conditions that involve marked drops in temperature. Some types of steel, such as austenitic stainless steel (see point 8.4), do not have this transition, while some carbon steels may have a ductile–brittle transition at temperatures close to 0 °C.

In terms of project design, material fracture under stresses lower than those found in the tables should be considered above all when the structure contains stress concentrators (drilled holes, chamfers, etc.). In particular, the fracture toughness of steel chosen for the most drastic environmental conditions (especially temperature conditions) to which it will be subjected should be considered. Careful planning can minimise the effects of stress concentration relating to discontinuities in the structure, closed angles and drilled holes. In general, the fracture toughness is greater in steels with a lower carbon content and more refined particles (see point 5). Tempering to relieve stress (heating and keeping steel at temperatures roughly between 250 and 400 °C, followed by slow cooling) can lead to increased steel toughness.

Analysing the fracture surface of steel makes it possible to determine the type of fracture quite easily. A fibrous fracture surface, with evidence of extensive plastic deformation, is linked to a ductile fracture, while a smoother, cleaner fracture is linked to a brittle fracture (see Fig. 6.5).

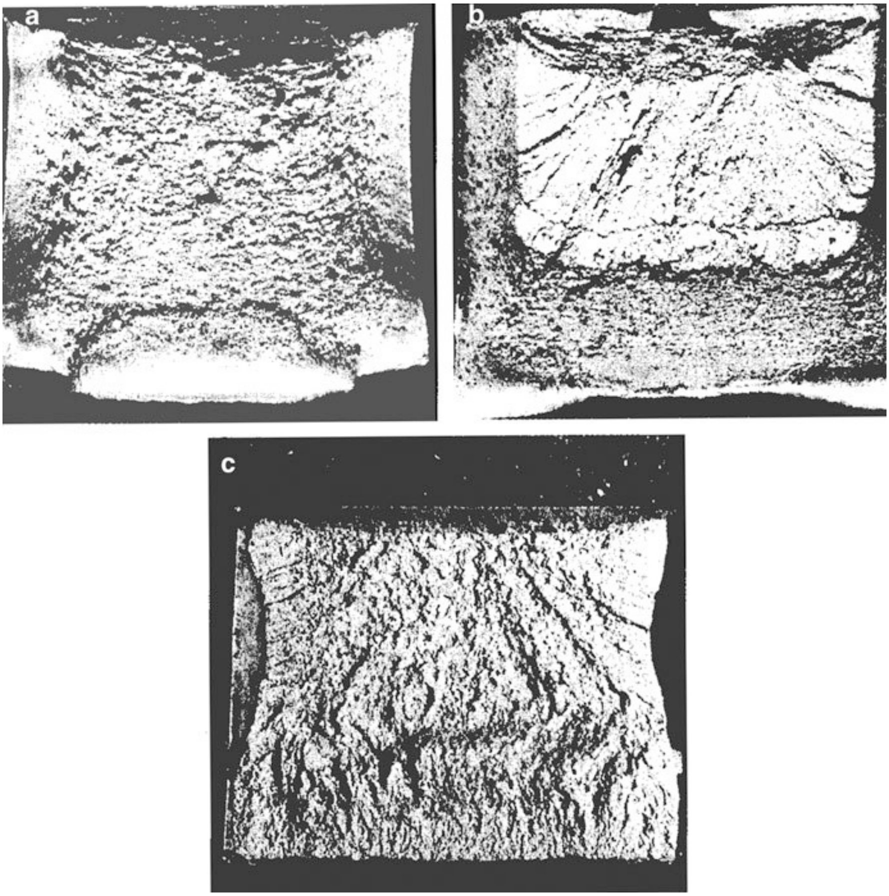
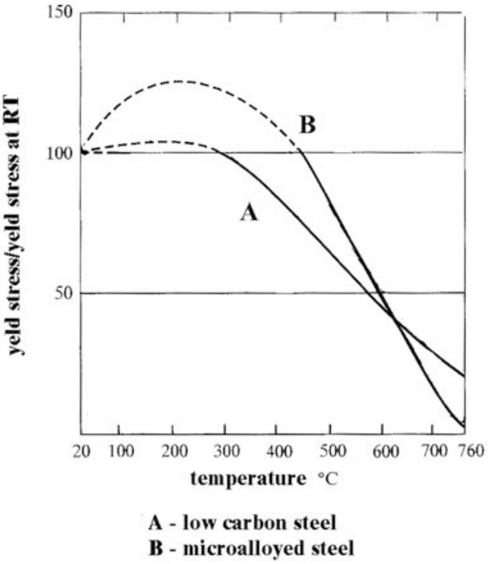


Fig. 6.5 Surfaces typical of fractures obtained in a Charpy test: (**a**) brittle fracture; (**b**) mixed fracture (ductile–brittle); (**c**) ductile fracture

6.3.4 Effect of Temperature

Steels' mechanical properties are greatly affected by temperatures. Temperatures of more than 500 °C may result in changes of the microstructure (see following point) and/or irreversible deformation when the material is subjected to relatively small forces, since the yield strength may decrease suddenly (see Fig. 6.6). Conversely, exposing steel to high temperatures may produce severe surface corrosion or erosion, which may cause the component to lose its functionality. The Young's modulus of steels, which is around 200 GPa at room temperature, falls to 170 GPa at 480 °C, decreasing quickly from that temperature upwards and causing the structure to lose stiffness.

Fig. 6.6 Variation in yield strength of carbon steel at different temperatures



Among the alterations to steel properties with increased temperature, prolonged exposure to fire may see a steel structure lose its capacity to sustain the structure and/or irreversible damage.

6.3.5 Variability of Mechanical Properties

Steels are perhaps among the construction materials with the greatest uniformity of properties. Nonetheless, some variations in the mechanical properties of a specific steel may occur in different sections of the same component or between components. The problem of variability in mechanical properties is, above all, due to small differences in the steel's chemical composition or small differences in its temperature or mechanical history during the manufacturing process.

As an example, see Fig. 6.7 for the distribution of ASTM A285 construction steel properties•. Naturally, although the spectrum of variation is relatively narrow, this type of variability should be taken into account both by suppliers and users with regard to quality control of the raw materials and project specifications.

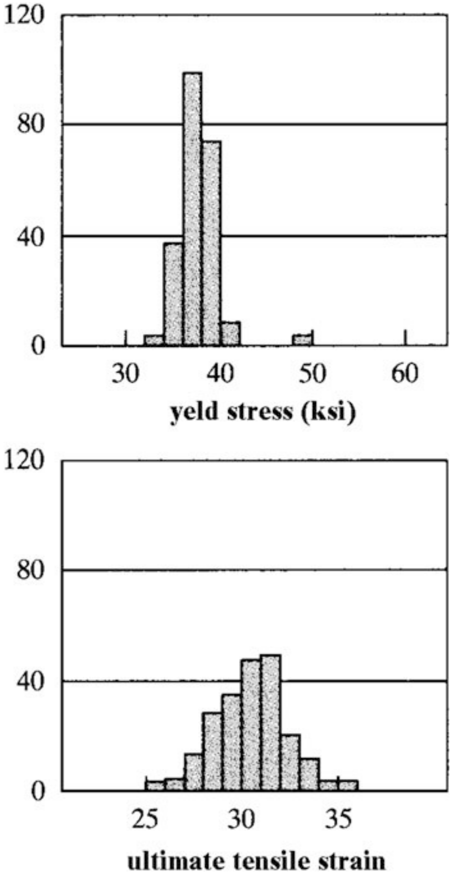


Fig. 6.7 Distribution of mechanical properties in a ASTM A285 steel sheet. The data refers to 224 steel sheets with these specifications bought from six suppliers over a period of 8 years (*source*: "Metals Handbook" (9th ed.), vol. 1. *Properties and Selection*: *Irons*, *Steels*, *and High-Performance Alloys*, ASM International, 1990, p. 195)

6.4 Effects of Alloy Elements

6.4.1 Carbon

Pure iron is fairly uninteresting in terms of its mechanical properties: it is overly soft, ductile and has little resistance to forces. Adding small amounts of carbon, however, radically alters its mechanical properties. By definition, the carbon content in steels cannot be greater than 2 % of mass• and generally, for structural steels, the carbon content is no greater than 0.3 %. Iron alloys with a carbon content higher than 2 % are known as cast iron and, although it is an important type of construction material, it will not be dealt with in this chapter.

Carbon atoms have a mass that is four-and-a-half times smaller than the mass of iron and a volume that is 26 times smaller. In terms of size, the difference between carbon and iron atoms compares to the difference in size between a tennis ball and a football ball. How can we understand, then, why adding such small quantities of an atom as apparently insignificant as carbon brings such great changes to iron's properties?

The first answer to this question lies precisely in the fact that carbon atoms are much lighter than iron atoms. This means that the proportionality of atoms is greater than the proportionality of mass. For example, a steel with 0.2 % percentage by mass of carbon has 1 % atomic percentage. Nevertheless, this is not enough to explain the accentuated effect that adding carbon has on iron.

Let us imagine a piece of wire (practically pure iron, since its carbon content in wire will not be more than 0.02 %) initially straight and then bent until the elastic limit of the material is exceeded. We can do it easily and when we do it we permanently alter the shape of the wire, which becomes bent. What happened to the iron atoms (which before were organised to form a piece of straight wire) when we bent the wire?

The answer, once again, lies in the metallic bonding and crystal structure of the phases that constitute the material. On the one hand, as mentioned before, metallic bonding is based on sharing free electrons by all atoms, which allows the iron atoms—arranged in atomic planes in the crystal structure—when they are subjected to force, to slide against each other without the material necessarily rupturing. On the other hand, crystal structures are not perfect, and there are several types of defects (lacunas, interstitial defects, grain boundaries, etc.). Among the defects that naturally exist in the crystal lattice of a metallic phase, there is one type that has a dramatic influence on the mechanical properties of a material, that is, dislocation, which is shown in Fig. 6.8. Simply put, the dislocation helps the atoms to slip over each other during plastic deformation. In this way, it is the movement and the generation of dislocations that, in general, control the material's yield (changing from an elastic deformation regime to a plastic deformation regime), the plastic deformation mechanisms and the behaviour of the material under plastic deformation. The shift from the elastic deformation regime (reversible deformation) to the plastic deformation regime (irreversible deformation) is a consequence of the start

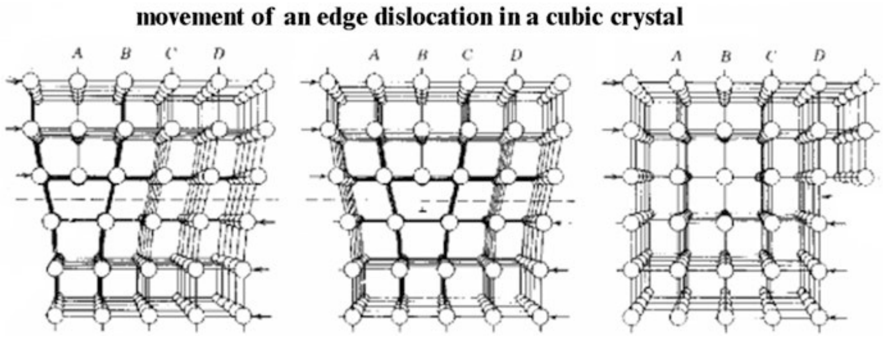


Fig. 6.8 Diagram of an edge dislocation (single) in a crystal lattice

of the movement of dislocations and the creation of new dislocations when yield strength is exceeded. The more difficult it is for these mechanisms to be activated, the greater the yield strength of the material and the greater its mechanical strength.

Now let us consider adding carbon to iron. Since the iron atoms are much larger than the carbon atoms, the latter may occupy the interstices between the iron atoms. The carbon atoms are now obstacles to the movement of dislocations: the more carbon atoms occupy the interstices in the iron's crystal structure, the more difficult is the dislocation mobility and greater will be the steel's yield strength ("mechanical strength"). As a result, and going back to the example of the wire, if we increase its carbon content, the force needed to bend it is greater. This mechanism is known as solid solution strengthening.

Iron's BCC structure, ferrite, is stable up to 911 °C, thanks to its spatial arrangement, and it can only dissolve 0.025 % carbon at the most. If a larger amount of carbon is introduced into the iron, we see the same phenomenon as when we put a lot of sugar in water: it precipitates. In steel's case, excess carbon precipitates to form an iron carbide: Fe_3C, known as cementite. This carbide is hard and brittle and its precipitation inside the ferrite matrix further increases the material's mechanical strength.

This mechanism for increasing mechanical strength arising from the precipitation of a second phase is naturally called precipitation strengthening or precipitation hardening. The more carbon there is, the greater the proportion of cementite, the greater the mechanical strength and the greater the difficulty to plastically deform the steel. These phases, one soft (ferrite, rich in iron) and the other hard and brittle (cementite, richer in carbon) can be easily observed using a microscope and form what is known as the steel's microstructure (see point 5 of this chapter). This mixed (biphasic) microstructure formed of ferrite and cementite acts in a way that can be comparable (although only loosely) to that of a composite material (e.g. a tennis racquet composed of a polymeric matrix strengthened with glass fibres).

6.4.2 Other Alloy Elements

As well as carbon, other alloy elements can be added that also help to change steel's properties or give it certain attributes. In spite of the high number of alloy elements that can enter steel's chemical composition, the design principle of a steel is relatively simple: there is an iron-rich matrix, which gives the material toughness, that is strengthened by dispersion of harder carbides. Thus, the elements that enter steels' composition can be divided into two groups: elements that form the matrix and elements that, together with carbon, form strengthening carbides.

As mentioned previously, the main component of a steel matrix is iron. Nevertheless, it was found that adding copper, nickel and cobalt to some steels, which helps to form the matrix, can improve certain specific properties. Adding up to 0.8 % Cu to construction steels leads to an increase in the material's resistance to corrosion and a change in the surface colour (which becomes brownish, after being put into use), an alteration that can be used for aesthetic purposes. Co increases the starting temperature for steel fusion, making it refractory (greater heat resistance). Nonetheless, adding Co tends to reduce the matrix's toughness and, generally, Co content in refractory steels should not exceed 5 %. It is not common to find commercial construction steels with significant Co content in their composition. Ni expands the austenitic region, which is extremely important in welded construction stainless steel (see point 7).

Other alloy elements, such as Mn, N and Si, can also be dissolved into steel's iron matrix in small quantities and contribute to solid solution strengthening. The strengthening that arises from adding alloy elements essentially depends on the difference between the size and electronic structure of the solute and solvent atoms, which in the case of steels are iron atoms. In diluted solid solutions, strengthening caused by solute atoms is approximately proportional to concentration. As mentioned earlier, the solute atoms distributed randomly over the crystal lattice of the solid solution make dislocation movement more difficult, which leads to an increase in the steel's yield strength. However, if the solute atoms are concentrated preferentially around displacements, they have a pronounced effect on stabilisation, thereby causing a substantial increase in the force needed for dislocation movements to begin.

In the 1950s, the metallurgists Gladman and Pickering developed semi-empirical equations that make it possible to estimate some of steels' mechanical properties, particularly yield strength, maximum uniform stress and ductile–brittle transition temperature, based on their chemical composition. For structural carbon steels (see point 8), the equations have the following form:

$$
\begin{aligned}
\sigma_{\text{yield}}(\text{MPa}) &= 53.9 + 32.3\,\%\text{Mn} + 83.2\,\%\text{Si} + 354\,\%\text{N} + 17.4\,\text{d}^{-1/2} \\
\sigma_{\text{mu}}(\text{MPa}) &= 294 + 27.7\,\%\text{Mn} + 83.2\,\%\text{Si} + 3.85\%(\text{perlite}) + 17.4\,\text{d}^{-1/2} \\
\text{TT}_{\text{ductile/brittle}}(^{\circ}\text{C}) &= -19 + 44\,\%\text{Si} + 100(\%\text{N})1/2 + 2.2\%(\text{perlite}) \\
&\quad - 11.5\%\text{d}^{-1/2}
\end{aligned}
$$

in which d is the grain size in mm, and N is the nitrogen content of the steel. Perlite will be defined in point 5.

The quantity and type of strengthening carbides present in the steel depend, naturally, on the steel's carbon content but also on the type of alloy elements that join it to form carbides. Further to the iron that forms cementite, (Fe_3C), as previously mentioned, carbide-forming elements (W, Mo, V, Nb and Cr) have different characteristics and can be divided into two groups: elements that form hard carbides (W/Mo and V/Nb) and Cr.

W and Mo have similar functions, and the choice of one or the other is essentially based on price. These elements form carbide η (M_6C), whose composition ranges between Fe_3W_3C and Fe_4W_2C, in the case of steels that only have W, or most commonly $(Fe, Mo, W)_6C$. Carbide η is not very soluble in the austenitic matrix and, as such, W and Mo contribute little to the steel's ability to be

Table 6.1 Alloy elements and typical functions in steel

Element	Typical functions
C, Ni, Co, Mn, Si, Cu, Cr	Formation of a solid solution (in which the solvent is iron) leading to an increase in mechanical strength (C, Ni, Mn, Si, Cu) or resistance to corrosion (Cr)
C, V, Mo, Nb, W	Formation of carbides (stoichiometric compounds formed of carbon and a metallic element) that help increase the hardness of steel and its resistance to softening when exposed to higher temperatures
Pb, S, P	Formation of a second phase that helps promote steel's machinability

strengthened through quenching. Adding vanadium or niobium to steel essentially aims to produce MC carbide. The MC particles are normally angular and are extremely hard, which significantly increases steels' abrasion resistance. On the other hand, the MC carbide precipitates at the grain boundaries, which stops coalescence of the grain during austenitisation (increasing the grain size). This makes it possible to obtain steels with a finer grain size, which simultaneously helps increase the steel's yield strength, toughness and weldability (see point 7).

Adding chromium to steel helps form carbides, increases steel's ability to be strengthened through quenching (see point 6.2), increases resistance to corrosion and delays ageing during tempering (see point 6.2). In construction steels, the chromium content does not normally exceed 1 %. This situation changes when steels with high resistance to corrosion are desired, so-called stainless steels (see points 7 and 8). In that case, the chromium content should be higher than 12 % so as to render the steel passive, stopping corrosion when it is exposed to the oxygen and moisture of the atmosphere.

A relatively wide range of other elements may appear in the composition of a steel as a result of the manufacturing and refining process (as is the case for P or Mn) or because small amounts are added deliberately with a view to obtaining certain benefits (such as Si). Conversely, depending on the content of each element, they may play different functions in steel, which leads to an extraordinarily diverse range of properties. Table 6.1 presents a summary of the range of elements that may be included in construction steel and their general functions.

6.5 Microstructure

In accordance with the chemical composition and temperature to which it is subjected, steel can have different microstructures, which correspond to different mechanical properties. Metallurgists and materials engineers systematise this information in diagrams, which they call phase diagrams. Figure 6.9 shows the phase diagram for iron—carbon in the Fe-rich region.

As previously mentioned, at 912 °C there is an allotropic transformation in which iron changes from a BCC structure to an FCC structure, austenite. Austenite

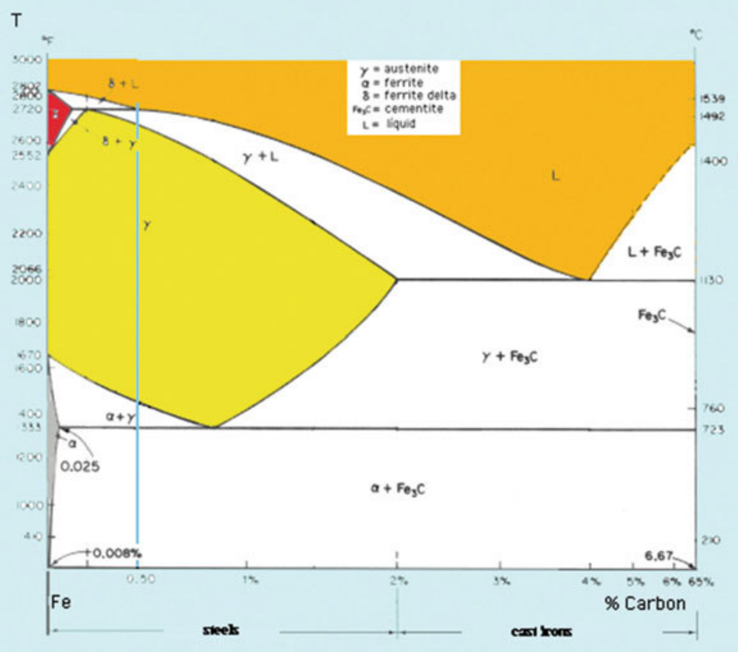


Fig. 6.9 Equilibrium Fe-C phase diagram

can dissolve 2 % carbon, almost 100 times more than ferrite. Therefore if a steel that has, for example, a carbon content of 0.5 % (see the vertical line in Fig. 6.9) and is heated to 1000 °C, all the carbides in it will disappear from its microstructure because the carbon will be dissolved by the iron-rich phase (if water-containing sugar precipitated at the bottom is heated, the sugar will disappear too). If the steel is then cooled slowly, the material follows the transformations shown in the phase diagram of Fig. 6.9. At around 750 °C, it will enter the austenite-ferrite biphasic region, which corresponds to the appearance of ferrite (since the austenite was already present). At 727 °C, the austenite still remaining disappears, becoming ferrite and cementite (Fe_3C). This transformation of austenite into ferrite and cementite during cooling is known as eutectoid transformation and leads to a very characteristic microstructure, which is shown in Fig. 6.10. This microstructure is formed of lamellas of ferrite and cementite, normally called perlite. In steels with a carbon content of up to 0.8 % (which is the case for most construction steels) that are cooled slowly, the proportion of perlite increases in line with the increase in carbon content, which corresponds to a trend towards increased yield strength in steel.

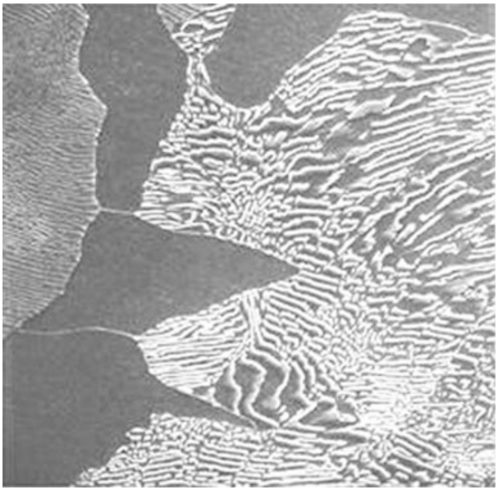


Fig. 6.10 Microstructure of a Fe-C steel (with 0.5 % C) cooled slowly from the austenitic region

6.6 Optimising Mechanical Properties

The reason for using steel as a structural material lies, as mentioned previously, above all in its strength and ductility. These properties essentially depend on the steel's chemical composition, temperature and mechanical history. These aspects will be dealt with briefly in this point.

6.6.1 Work Hardening

Once the yield strength of a metal alloy has been exceeded, the atoms start to slide over each other because of movement and create dislocations, which leads to permanent deformation of the material, known as "plastic deformation". As plastic deformation continues, the density of dislocations increases and a more and more complex network of dislocations arises in the material's crystal lattice. The increase in the density of dislocations makes its movement more and more difficult, since they begin to interact with each other. This means that plastic deformation in steel (and metal alloys in general) at room temperature does not occur at a constant stress, as mentioned in point 3.2, i.e. steel undergoes work hardening.

The work hardening of metal alloys, and steel in particular, has an important consequence: mechanical strength can be increased through pre-deformation above the yield threshold (Fig. 6.11). By doing this, the material's yield strength is no longer the initial strength but rather the highest achieved in the previous deformation. This mechanical process is used frequently for construction steels and is sometimes known as pre-deformation or pre-stressing, and leads to an increase in the material's yield strength.

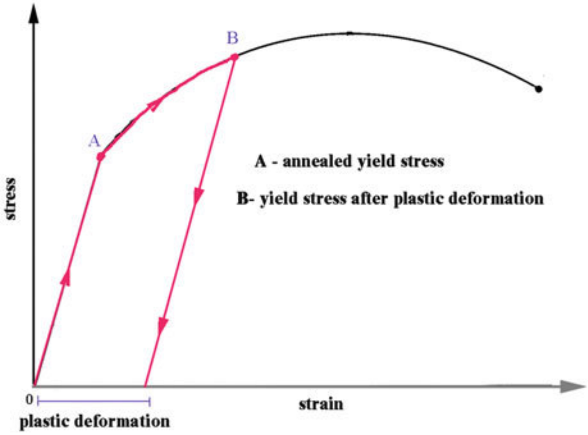


Fig. 6.11 Pre-deformation of steel

In terms of pre-deformed steels, it is important to consider two aspects. On the one hand, pre-deformation also leads to lower toughness of the steel, i.e. its energy absorption capacity when subjected to violent impacts. On the other hand, a pre-deformed steel, when subjected to temperatures of several hundred degrees (normally between 300 and 600 °C), recrystallises; simply put, the network of displacements created during plastic deformation that the material underwent is eliminated. As a result, the yield strength of the material returns to its initial value: the material softens. In this way, pre-stressed steels are difficult to weld because softening occurs around the welding joint, together with a reduction in the material's mechanical properties.

6.6.2 Heat Treatment

Heat treatments can be defined as a set of operations that involve heating and cooling the material, in solid state, with a view to obtaining a specific microstructure and optimise a certain set of the material's properties (mechanical or otherwise).

Structural carbon steels are generally used in a tempered or standardised state, that is, their microstructure corresponds, broadly speaking, to an equilibrium microstructure, described in point 5. Nevertheless, to obtain a certain range of properties, it may be necessary to subject the steel to quenching and tempering. For construction steels, this is valid particular in the case of alloy steels described in point 8.3. As such, it is important to briefly describe heat treatment.

If, starting at a temperature in which steel is formed only by austenite, which depends on its chemical composition but is typically around 1000 °C (see diagram in Fig. 6.8), steel is cooled quickly to room temperature, the carbon does not have time to precipitate: it remains trapped in the iron's crystal lattice, distorting it. This phase, with the "distorted" crystal structure, is martensite. Heat treatment that

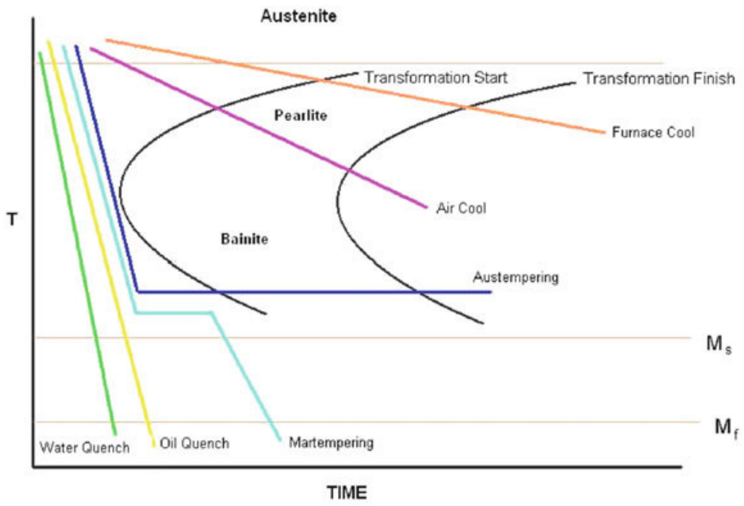


Fig. 6.12 TTT diagram of a Fe-C steel (with 0.8 % C)

consists of raising the temperature of the steel to austenitisation temperature and then quickly cooling it to room temperature (e.g. by submerging the piece in water, oil or a salt bath) is known as quenching. And it is because they were subjected to this treatment that we are not able to bend or break the steel blades of the butchers' knives or of swords. They are hard, to be able to resist wear in the cutting area, but they are also brittle: their microstructure is martensitic. The appearance of martensite leads, therefore, to increased hardness and yield strength of the steel, but makes it more brittle.

If the cooling rate after austenitisation is greater than a certain critical rate (which depends on the material's composition), martensite is formed. This critical rate (the cooling speed to which steel must be subjected to stop carbon and other alloy elements diffusing, leading to an oversaturated solid solution known as martensite) depends on the steel's chemical composition. Metallurgist engineers collect that information in diagrams similar to the one in Fig. 6.12, which are known as TTT diagrams (time, temperature, transformation). These diagrams, simply put, consist of two curves in C and two horizontal lines. The curves in C represent the start and end of diffusion transformations (which lead to equilibrium phases: ferrite and carbides), while the horizontal lines define the start and end of the martensitic transformation (known, respectively, as M_s and M_f temperatures). If we want to quench the steel, the cooling speed will have to be such that the C curves are not intersected by the cooling curve (see Fig. 6.12). In this way, the further to the right the steel's C curves, the easier it is to quench, and this is why the steel is said to have a greater ability to be strengthened through quenching.

Alloy elements can be divided into alphagenic and gammagenic elements according to how the ferrite region and austenitic regions expand, respectively. All carbide-forming elements are alphagenic, except for Mn, while carbon and all

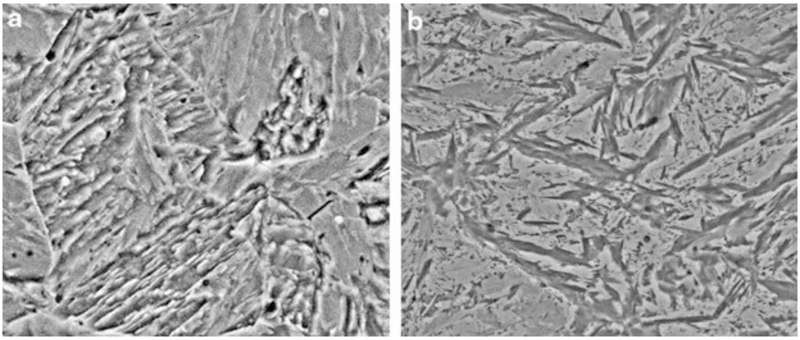


Fig. 6.13 (**a**) Martensite with low carbon content (lath martensite); (**b**) martensite with high carbon content (plate martensite)

elements that form the matrix are gammagenic. It is the balance between alphagenic and gammagenic elements and the content of alloy elements that control the M_s and M_f temperature, the ability for the steel to be strengthened through quenching and the type of carbides that arise (during solidification and cooling, in heat treatments such as tempering). Generally speaking, all the alloy elements except Co increase steel's ability to be strengthened through quenching, pulling the C curves to the right. The power of each element to encourage that ability varies. The series of elements that follows is organised in descending order in terms of the alloy's effect on steel's ability to be strengthened through quenching: $C > V > Mo > Cr > Mn > Si > Cu > Ni$. Conversely, the amount of martensite obtained after quenching also depends on the characteristic M_s temperature of the steel. All alloy elements lower the M_s temperature.

The hardness of martensite is greater the higher the carbon content. The morphology of martensite also depends on carbon content, and it is known as lath martensite if it has a low carbon content (typically $C > 0.5$ %) and plate martensite if it has a medium/high carbon content (see Fig. 6.13).

The tempering of a steel is a heat treatment that consists of heating to temperatures between 300 and 550 °C (depending on the steel's composition), which is later quenched. This treatment makes it possible to eliminate remaining austenite, which arises if the M_f temperature is lower than room temperature, and to optimise the compromise between the material's hardness and toughness. During tempering, the alloy elements may diffuse, leading to the precipitation of very fine carbides in the martensite, which normally leads to lower material hardness but it increases its toughness, since martensite is an excessively brittle phase, as previously mentioned. For steels with a Cr content of more than 8 %, the material's hardness does not decrease significantly when tempered at temperatures up to 500 °C. This resistance to tempering is caused by precipitation of the carbide Cr_7C_3. Adding V and Mo allows the steel's resistance to tempering to be increased. These types of temper resistant steel are particularly useful for situations where there is a high chance of it reaching relatively high temperatures when in service.

6.7 Welded Construction

Welded construction is one of the major methods available to civil engineers to join steel components and create support structures. The principle of welding is relatively simple: the components are joined together and the join area is melted. Subsequent solidification removes the gap between the two surfaces, effectively joining the components.

The most common welding methods for steel civil construction structures are electric arc welding or passing an electrical current between two points (contacts) placed between the components to be joined (electric resistance welding). In both proceedings, the dissipation of electrical energy causes an increase in temperature, and localised fusion occurs in the area that the current passes through.

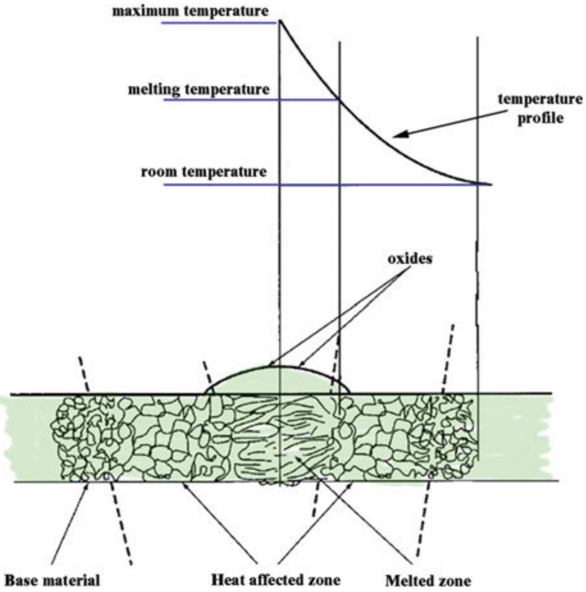
Welding processes, particularly electric arc welding processes, can occur by adding a third metal alloy. Adding this third material normally aims to locally change the properties of the welding joint, increasing the pair's weldability.

Since, in welding, fusion is localised, there is always a temperature gradient between the melted area (fusion zone), whose temperature is higher than melting point, and the areas of the component that are further away from the fusion zone, which will have lower temperatures. On the other hand, because, in general, the volume of the fusion zone is small compared with the volume of the components to be welded, and since the latter have high thermal conductivity, the mass of the components work to channel away the heat. These two factors mean that the cooling rates for steel welding are quite high (typically between 10^2 and 10^5 °C/s). Temperatures higher than melting point, temperature gradients and high cooling rates inevitably mean that the steel's microstructural characteristics are changed (and its properties are therefore altered too) in the area around the welding joint. These changes are conditioned essentially by the steel's composition, its temperature and mechanical history, and the process and parameters of welding used (that limit the welding's temperature conditions: maximum temperatures, temperature gradients and cooling rates). On the other hand, the heating and cooling cycles during welding lead to shrinkage and expansion of the component, as a result of temperature variation and phase transformations that steel can undergo between room temperature and melting point (see point 3), thereby making it possible for warping to appear in the structure, weakening the joint or causing cracks to appear.

It is important to note, however, that if welding is performed carefully, it is a simple joining method that is not expensive and is as reliable—and perhaps more so—than any other process, particularly in comparison with riveting. The main parameters to be taken into account in construction steel welding will now be discussed.

Observing the cross-section of a welded steel joint (Fig. 6.14) makes it possible to identify, generally speaking, three different areas: the base metal (BM); the heat-affected zone, where reactions only take place in solid state (HAZ), i.e. where the temperature range went from room temperature to steel melting point; and the fusion zone, where the steel's meting temperature was exceeded (FZ).

Fig. 6.14 Representation of the cross-sect. of a welding joint, showing the fusion zone (FZ), the heat-affected zone (HAZ) and the base metal (BM)



In the HAZ, even if the welding process uses an added metal, the composition of the material is not changed. There may be several microstructural alterations, however. Three of them should particularly be taken into consideration when selecting steel for welding:

- **The precipitation of intermetallic compounds** (normally carbides) and subsequent decrease in the content of alloy elements in solid solution in the matrix. In the case of austenitic stainless steels, this problem can be minimised by reducing the carbon content, for example, using the so-called ELC (extra low carbon) steels.
- **Grain coalescence/recrystallisation**. An increase in grain size always means reducing the toughness of the material, which may lead to a brittle fracture under sudden variations in load conditions (impacts) or heat conditions (see point 3). Adding small amounts of titanium, niobium or vanadium stabilises the grain size and improves the material's weldability. This is one of the advantages of using microalloyed steels with these elements to build welded support structures.
- **Heating to temperatures above austenitisation**, followed by a fast cooling rate that may, as already mentioned, result in the formation of martensite. Since martensite is a hard but brittle phase, its formation in the HAZ inevitably involves making the component more brittle close to the welding joint and may lead to cracking in the joint around this zone (normally known as cold cracking). The formation of martensite can be minimised by choosing a steel with a carbon content of less than 0.25 % (see the definition of equivalent carbon content later on), or by subjecting the component to be welded to pre- or post-heating in order to reduce the cooling rates during welding, thereby avoiding the formation of martensite.

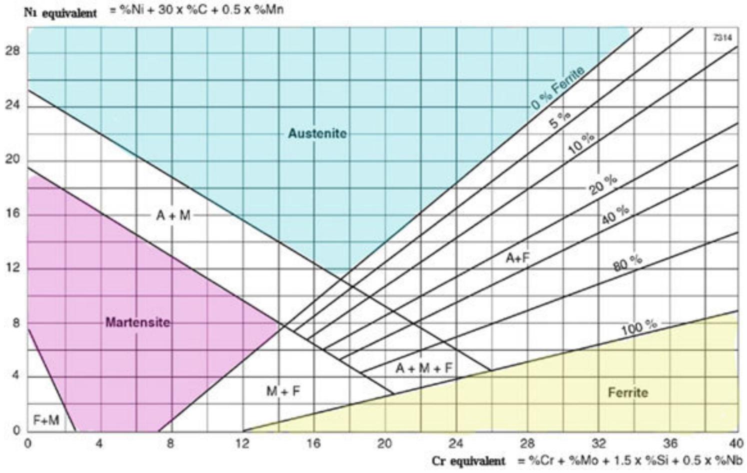


Fig. 6.15 Schaeffler diagram

The FZ's microstructure depends on the material and processing conditions. It is normally a microstructure formed of fine, elongated grains, known as a columnar-dendritic or columnar-cellular structure.

The phases present in this zone are not necessarily the same ones that the material had before the welding process, since the conditions for solidification are relatively drastic. Predicting the phases present in the welded joint, which naturally have an impact on the joint's properties, can be done by using the Schaeffler diagram (Fig. 6.15).

In this diagram, steel's composition is transformed into nickel and chromium equivalents (see Fig. 6.15), which make it possible to establish a point on the diagram that corresponds to a certain type of structure. Normally the formation of martensitic or ferritic structures that could embrittle the joint is avoided.

In relation to the FZ, another important aspect should be noted: since solidification starts in the (cooler) HAZ solid material, ending close to the centre of the joint where the two solidification fronts meet, it is in this region that the elements with lower melting points tend to concentrate, and they may become part of the steel's composition, particularly sulphur and phosphorus. In this way, the presence of these elements considerably reduces steels' weldability, since they may cause brittle sulphide or phosphite films to form, leading to cracking of the welded joint (normally called hot cracking).

The greater or lesser ease with which a certain steel can be welded is known as weldability. Weldability is a vague concept that is difficult to quantify, and involves the aspects mentioned above (and others that were not referred to here, such as a change in resistance to corrosion, embrittlement by hydrogen, etc.), but generally it can be said that a steel's weldability decreases as the steel's carbon content increases. A simple and commonly used way of estimating a steel's weldability and, in particular, the influence of the alloy elements on the steel's weldability is by applying the concept of equivalent carbon content (CE):

$$\begin{aligned} \mathrm{CE} = {} & \%\mathrm{C} + (1/6)(\%\mathrm{Mn}) + (1/5)(\%\mathrm{Cr} + \%\mathrm{Mo} + \%\mathrm{V}) \\ & + (1/15)(\%\mathrm{Cu} + \%\mathrm{Ni}). \end{aligned}$$

For a steel to be "weldable" or at least "weldable on site" without the need for special methods, precautions or risks, the CE value must not exceed 0.25 %. If it is greater than this value, the cooling conditions and added metal must be controlled and the welding method should be chosen carefully to avoid the risk of cracking or embrittlement of the structure.

Finally, it should be mentioned that welding can also influence the component's resistance to fatigue due to the possible formation of microcracks, pores or microinclusions of slag in the welding joint. As such, it is indispensable that the joints in welded structural elements are subjected to rigorous quality control. As well as macroscopic inspection, perhaps using liquid penetrant inspection, the fact that welding defects may be subsurface means that ultrasonic and radiographic testing must be carried out.

6.8 Main Types of Steel Used in Civil Engineering: Uses and Properties

As mentioned previously, different types of steel have been developed to meet different specifications and service conditions (high loads, wear, impact, atmospheric corrosion, high temperatures, etc.). As well as the chemical aspect, the same steel can be subjected to different heat or mechanical treatments that alter its properties. In this way, choosing the right steel for a specific use can be a relatively complex task, in which several factors must be considered: the properties required (which are sometimes apparently contradictory, such as high hardness and high ability to withstand impacts, for example), the sizes and shapes available, cost, etc.

One way for a project engineer to deal with this diversity of options and the complexity inherent to choosing the right material is consulting databases and catalogues in which the steels available are grouped, making sets with a certain, or several certain, example uses. These databases typically have between 12 and 20 main groups of steels (construction steels, stainless steels, spring steels, tool steels, quick steels, etc.), which can then be divided into more specific subgroups. Once the group corresponding to the desired use has been identified, the steel best suited to the project's specifications can be chosen.

In the particular case of construction uses, it is interesting to note that until the middle of the 1960s, with the exception of building bridges, practically only one type of steel was used. This steel was normally classified as carbon steel and international standards specified only its minimum yield strength as 230 MPa. Other steels with specific properties, such as resistance to corrosion or weldability, were available (which was the case for ASTM A242 or ASTM A373) but they were rarely used for buildings.

Currently, an enormous range of construction steels are available for project designers, allowing them to increase strength in certain areas without excessively increasing the volume of the components, increase resistance to corrosion and subsequently the structure's durability, reduce (or even eliminate) the frequency of painting, etc. A description of the four main groups of steels currently used in construction follows: carbon steels, microalloyed steels, quenched and tempered alloy steels and stainless steels. Naturally, this description is brief and merely aims to illustrate the main types of steel used in construction, their characteristics and uses.

6.8.1 Structural Fe-C Steels

Despite their name, carbon steels contain other alloy elements as well as carbon. The name is used for steels with an alloy element content levels that are lower than the following: carbon <1.7 %, manganese <1.65 %, silicon <0.6 % and copper 0.6 %. This category includes steels known as mild (carbon <0.15 %) up to high carbon steels (0.6 % $<$ carbon $<$ 1.7 %). Carbon steels used in structures normally have carbon content levels of between 0.15 and 0.30 %. These steels can be used generally in riveted or welded structures and have yield strengths of around 275 MPa. Increasing the carbon content increases yield strength but also reduces the steel's toughness and weldability, as mentioned previously.

6.8.2 High Strength Microalloyed Steels

These steels are sometimes known as HSLA—high strength low alloy—steels and can have yield strengths of between 275 and 500 MPa. Unlike carbon steels, where increases in strength are achieved by increasing carbon content, in HSLA steels this is achieved by adding small amounts of alloy elements, such as chromium, manganese, molybdenum, niobium, nickel, vanadium or zirconium. Adding these elements causes solid solution strengthening and precipitation strengthening caused by fine dispersions of carbides and leads to a refinement of the steel microstructure. The result of this is an excellent compromise between high yield strength and ductility, a compromise that cannot be achieved in carbon steels. Due to its high toughness and the fact that precipitates stabilise grain size during heating, these steels generally have good weldability, and are particularly suitable for welded construction.

6.8.3 Quenched and Tempered Alloy Steels

As previously mentioned, quenching steel increases hardness and consequently increases the steel's yield strength.

Quenching low alloy steels may produce materials with yield strengths of between 550 and 800 MPa. However, after quenching, steels become brittle, which means some special care must be taken when using them in welded construction, and some special care must be taken by the project designer because the energy absorption capacity of these materials may be small (the analogy with stretched elastic mentioned previously should be remembered here). In order to reduce the brittleness of quenched steels, after it has been quenched, the steel is tempered at temperatures between 400 and 600 °C in order to encourage some diffusion of the carbon trapped in the martensitic structure, thereby reducing the intrinsic brittleness of this phase. These steels are therefore normally used in their quenched and tempered state.

6.8.4 Stainless Steels for Welded Construction

There are three main groups of stainless steels: martensitic stainless steels, ferritic stainless steels and austenitic stainless steels, defined according to the dominant phase in their constitution at room temperature. In welded construction for civil engineering structures, particularly piping for aggressive fluids, austenitic stainless steels (of the well-known 3XX series) are the most frequently used, due to their good compromise between mechanical strength, resistance to corrosion and weldability.

Austenitic stainless steels have a microstructure that at room temperature is formed essentially of grains of austenite. This is possible because some elements of the alloy, such as nickel and manganese, expand the FCC (austenite) phase and, if added in sufficient quantity, may retain this phase, stabilising it at room temperature. This phase has high ductility, and may undergo solid solution strengthening. Furthermore, austenitic steels do not have a ductile–brittle transition. In turn, chromium allows the steel's resistance to corrosion to be significantly increased. When the chromium content is higher than 12 %, a fine, stable film of chromium oxide forms on the surface of the steel, which protects the iron from reacting with the atmosphere, particularly reactions that lead to the formation of oxides, commonly known as rust. This is how the steel becomes stainless.

6.8.5 Summary of Properties

Tables 6.2 and 6.3 show the typical properties of some of the steels that are most commonly used in civil engineering. Table 6.2 includes structural carbon steels, high resistance microalloyed steels and quenched and tempered alloyed steels, while Table 6.3 shows the specifications of some stainless steels. The aim of

Table 6.2 Specifications and properties typical of steels common in civil construction

		C and Mn content		Mechanical characteristics (MPa)		
ASTM designation	Type	%C	%Mn	σ_{yield}	σ_{um}	Typical shapes available
A36	Structural carbon steel	0.26	–	250	400–550	Plates and beams with different cross-sections
A529	Structural carbon steel	0.27	1.2	290	415–484	Plates, sheets, bars and beams
A242	High resistance microalloyed steel (good resistance to corrosion)	0.15	1.0	290–345	435–480	Beams and plates with specific shapes
A572	High resistance microalloyed steel	0.21	1.35	290	415	Different components and shapes
A588	High resistance microalloyed steel (good resistance to corrosion)	0.17–0.19	0.5–1.25	290–345	435–485	Varied shapes and sizes
A514	Quenched and tempered alloy steel	0.12–0.21	0.4–1.1	290–690	690–895	Most of all plates

Table 6.3 Stainless steels

		Content C, Ni and Cr			Mechanical characteristics (MPa)	
ASTM designation	Type	%C	%Cr	%Ni	σ_{yield}	σ_{mu}
410	Martensitic stainless	0.08–015	11.5–13.5	–	–	–
430	Ferritic stainless	0.08	16–18	–	260	450–600
304	Austenitic stainless	0.05	17–19.5	8–10.5	230	540–750

Table 6.4 Maximum values for non-alloy steels

Element	Maximum value (%mass)
Al	0.30
B	0.0008
Bi	0.10
Co	0.30
Cr	0.30
Cu	0.40
Ca	0.10
Mn	1.65
Mo	0.08
Nb	0.06
Ni	0.30
Pb	0.40
Se	0.10
Si	0.60
Te	0.10
Ti	0.05
V	0.10
W	0.30
Zr	0.05
Others (except C, P, S and N)	0.10

these tables is not to be exhaustive, and consulting manufacturers' catalogues provides more detailed and exhaustive information on the properties, shapes and prices of the specifications available. These tables merely aim to give an overall idea of the spectrum of steel properties that are currently used most often in civil construction.

ASTM A36 is a steel for general use, and is probably the most commonly used steel for constructing buildings and bridges, together with A529. Steel A529 is a microalloyed steel with vanadium, while steels A242 and A588 are microalloyed steels with greater resistance to atmospheric corrosion. Steel A514 is an alloy steel with Cr and Mo that can be quenched and tempered.

Table 6.3 shows some characteristics of three stainless steels, showing the groups of martensitic, ferritic and austenitic stainless steels. Thanks to its greater weldability, toughness and the fact it does not undergo ductile–brittle transition, austenitic stainless steels, from the 3XX series, are the most widespread in civil construction structures, particularly in welded construction, and have, as previously mentioned, high resistance to corrosion, particularly atmospheric corrosion.

6.9 Portuguese Standards

This point contains a short summary of the main Portuguese standards relating to the designation, classification and characterisation of steels.

Table 6.5 Maximum values for chemical composition between quality and special steels

Element	Maximum value (%mass)
Cr	0.50
Cu	0.50
Mn	1.80
Mo	0.10
Nb	0.08
Ni	0.50
Ti	0.12
V	0.12
Zr	0.12

NP EN 10027-1 (**1993**): Structure of steels and main symbol designation.

NP EN 10027-2 (**1993**): Structure of steels and main symbol designation (continuation of NP EN 10027-1).

NP 4379 (**1999**): Designation system for steels, additional symbols. This standard complements NP EN 10027-1. It covers additional symbols for designating steel, when they are not enough to provide a complete abbreviated identification for the steel or steel product.

NP EN 10020 (**2002**): Definition and classification of grades of steel: This standard defines the term "steel" and classifies the grades of steel.

Steel: Material which contains by mass more iron than any other single element, having a carbon content generally less than 2 % and containing other elements. A limited number of chromium steels may contain more than 2 % of carbon, but 2 % is the usual dividing line between steel and cast iron.

Non-alloy steels: Steels in which none of the contents reaches the maximum values in Table 6.4.

Alloy steels: Steels with a value for one of the alloy elements of more than the maximum values in Table 6.4.

Stainless steels: These are steels with at least 12 % chromium and a maximum of 1.2 % carbon.

Non-alloy quality steels: These steels generally have specific property requirements, such as toughness, grain size control and/or deformability.

Non-alloy special steels: These steels have a high purity level (P and S less than 0.02 %) compared with the previous types of steel (particularly in relation to the inclusion of metals). They are designed for total or partial quenching or tempering heat treatment. Precise control of chemical composition and special care in manufacturing and process control ensure improved properties to meet exacting requirements.

Alloy quality steels: These steels generally have specific property requirements, such as toughness, grain size control and/or deformability. Alloy quality steels may be intended for quenching, tempering or surface hardening.

Alloy special steels: This class includes steel grades other than stainless steels which are characterised by precise control of chemical composition and manufacture. They include alloy engineering steels and alloy steels for pressure vessels, bearing steels, tool steels, high-speed steels and steels with special physical properties. Table 6.5 shows the maximum values for the chemical composition of quality and special steels.

Conclusion

In terms of its use in civil construction, the introduction of steel as a structural material profoundly altered the methods and limits of construction up to that point, and had an enormous impact on the practices of civil engineering and architecture. Curiously, in the author's opinion, the knowledge transmitted when training construction specialists and technicians on the characteristics of this material is generally lacking, and is limited to little more than providing tables of properties and shapes available on the market and introducing catalogues. It is therefore difficult for specialists to explore new limits for using steels, make rational choices of the most suitable material for a certain use, or simply be aware of the problems arising from use of the material (fatigue, embrittlement, corrosion, etc.). It is possible that steel is, even today, a construction material that is under-exploited by engineers and project designers.

This chapter intended, above all, to briefly call attention to some of the aspects of the physical metallurgy of steels that most condition their properties, and it is hoped that consulting catalogues and choosing alloys can be done in a more structured manner in the future.

Acknowledgements I would like to thank Professor António de Pádua Loureiro for all that he has taught me about the physical metallurgy of steels many years ago during my undergraduate studies at IST.

Bibliography

ASM International (1990) Properties and Selection: Irons, steels, and high-performance alloys. Metals handbook (9th ed.), vol. 1, ASM International

Dieter GE (1988) Mechanical metallurgy, 3rd edn. McGraw-Hill Book Company, New York, NY

Grong O (1994) Metallurgical modelling of welding. Institute of Materials, London

Honeycombe RW, Badeshia H (1995) Steels: microstructure and properties, 2nd edn. Edward Arnold, London

Llewellyn DT (1992) Steels: metallurgy and applications, 2nd edn. Butterworth Heinemann, Oxford

Seabra AV, Loureiro AP (1981) Curso de Tratamentos Térmicos dos Aços, vol 1 and 2. Ordem dos Engenheiros, Lisbon

Sinha AK (1989) Ferrous physical metallurgy. Butterworths, London

Somayaji S (2001) Civil engineering materials, 2nd edn. Prentice Hall, Englewood Cliffs, NJ

Taylor GD (2000) Materials in construction: an introduction, 3rd edn. Pearson Education, London

Ceramics

7

Joaquim Valente de Almeida

Abstract

There are many ceramic products for construction and they are broadly used all over the world. They range from bricks for masonry to finishing materials. Ceramic technology has evolved greatly from the past to today and is the result of the evolution of the products themselves. To gain the desired results and more complex, demanding products, there needed to be an upgrade in technology.

The chapter will discuss only the main ceramic construction products:

- Clay bricks
- Clay roof tiles
- Ceramic wall and floor tiles

The sections will provide a general overview of the manufacturing process; the regulations applicable, including specifications, tests and CE marking for each of the products; and the most common problems linked with ceramic products (those that are intrinsic to the products and not how they are used).

Keywords

Clay bricks • Clay roof tiles • CE marking • Wall and floor tiles • Regulations • European standard • Manufacturing process • Testing standards • Problems

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M.C. Gonçalves, F. Margarido (eds.), *Materials for Construction and Civil Engineering*, DOI 10.1007/978-3-319-08236-3_7

7.1 Introduction

It can be said that the use of ceramic products in construction is as old as the human race.

There are many ceramic products for construction and they are broadly used in our civilisation's everyday life. They range from bricks for masonry to finishing materials (wall coverings, flooring and bathroom products).

Ceramic technology has evolved greatly from the past to today, and is the result of the evolution of the products themselves. To gain the desired results and more complex, demanding products, there needed to be an upgrade in technology.

Today, advanced ceramic construction products are being studied, including solar linings and solar clay roof tiles (by applying photovoltaic cells). Ceramic products are evolving to keep up with the trends in innovation in today's world, helping contribute to the sustainability of construction.

This chapter will discuss only the main ceramic construction products:

- Clay bricks
- Clay roof tiles
- Ceramic wall and floor tiles

The following sections will provide a general overview of the manufacturing process; the regulations applicable, including specifications, tests and CE marking for each of the products; and the most common problems linked with ceramic products (those that are intrinsic to the products and not how they are used).

The installation and use of ceramic products will not be covered in this chapter, but it is nevertheless a highly important topic, as most defects in ceramic products commonly arise due to their (incorrect) installation and use.

Much of this chapter is based on publications by APICER, coordinated by the CTCV (Technological Centre for Ceramic and Glass)—*Brickwork Manual* [1], *Clay Roof Tile Application Manual* [2] and *Ceramic Covering Use Manual* [3]. These monographs should be consulted to complement the information given here so that the reader can gain a better understanding of how the products are used in construction.

7.2 Clay Bricks

7.2.1 Manufacturing Process

This section begins with a general description of the different stages of the manufacturing process of clay bricks, from raw material to final packaging [1] Fig. 7.1.

Raw materials. In order to create a high-quality product, it is fundamental that the raw materials have appropriate characteristics and that they remain consistent over time. Since clay is a natural raw material, its characteristics can change over time. To try to minimise these changes, two types of clay with different

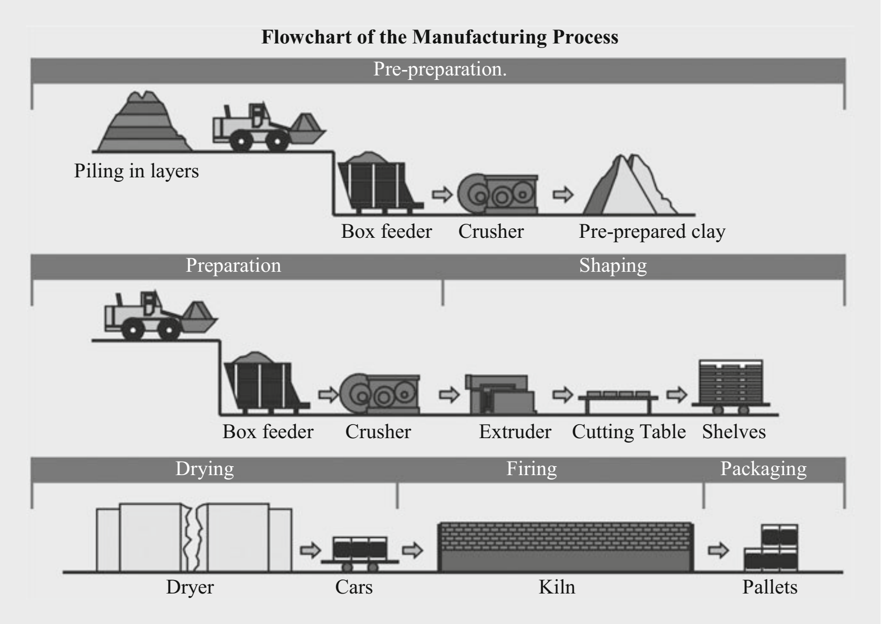


Fig. 7.1 Flow chart of the manufacturing process [1]

characteristics are normally used for brick manufacturing—one clay is more plastic (fat) and the other less plastic (lean). The amount of each to be used is decided, in order to create a mixture with consistent characteristics. The different clays are extracted during drier months and are left in the open air, in piles with interspersed layers and in large quantities, usually enough for up to a year's worth of consumption. This process allows the material to disaggregate and makes it easier to keep uniform.

Pre-preparation. The piles are cut vertically, passing through the different layers, and the clay is prepared in crushers—machines that consist of two rotating metal cylinders, which form small layers of mixture, thereby reducing its grain size. Pre-preparation of the mixture is fundamental to ensure that the process is stable, in terms of reducing breaking. After pre-preparation, the mixture is stored indoors, to protect it from outdoor weather conditions.

Preparation. The preparation stage generally consists of a second crushing. The mixture is then mixed with water to guarantee even conditions of moisture and plasticity.

Shaping. In the shaping stage, the mixture is passed through extruders, which are machines that force the mixture through brick-shaped moulds. During this stage, the mixture is vacuumed to remove the air inside it and give it better qualities. After extrusion, the material is cut to the desired dimensions and placed on shelves.

Drying. After shaping, bricks are dried in chambers heated to temperatures varying between 30 and 70 °C. This is a very delicate operation and should be controlled to minimise the problems that are inherent to the process (cracking). Drying time varies, depending on the composition of the mixture and the technical conditions used.

Firing. After drying, bricks are fired in tunnel kilns at temperatures that normally range between 800 and 1,000 °C. The firing cycle and temperature are variable and depend on the composition of the mixture. Controlling the firing conditions and adapting the firing parameters to the raw material properties and desired characteristics of the final product is fundamental to ensuring that the final product has the specifications desired.

Packaging. After firing, bricks are packed on pallets and protected by plastic film to make them easier to transport.

7.2.2 Regulations Applicable (Specification and Testing)

The following European standards are applied to clay bricks:

- European Standard EN771-1 [4]—specification standard.
- European Standards EN772—testing standards.

7.2.2.1 European Standard EN771-1

European Standard EN771-1 introduces the specifications to be met by clay bricks and classifies them according to their characteristics Fig. 7.2. Therefore clay bricks may be classified as belonging to one of the following two groups:

- LD Bricks:
- Clay bricks with a gross dry density lower than or equal to 1,000 kg/m^3 for use in protected masonry.
- HD Bricks:
- Clay bricks with a gross dry density higher than 1,000 kg/m^3 for use in unprotected masonry.
- Bricks for use in unprotected masonry.

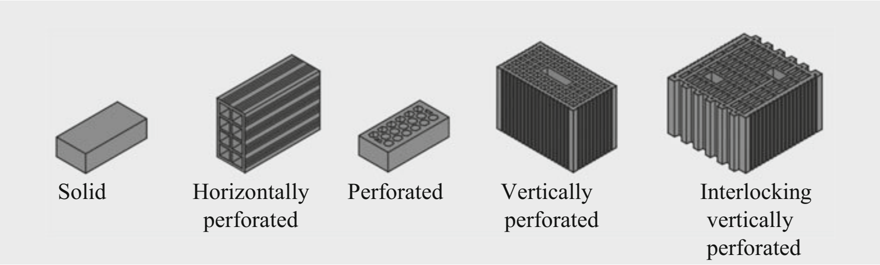


Fig. 7.2 Some examples of clay bricks [1]

In terms of use, clay bricks can be classified as:

- Facing—bricks that are designed to be exposed, inside or outside the building.
- Non-load bearing—bricks that do not bear any loads other than their own weight.
- Load bearing—bricks that have a structural role in the building.

Standard EN771-1 [4] establishes the requirements and tests applicable to clay bricks. For most requirements, the standard does not give defined criteria but rather the tolerances (classes), and it is up to the manufacturer to specify its products' characteristics.

The characteristics indicated should be established in accordance with the testing standards shown in Tables 7.1 and 7.2.

7.2.2.2 European Standards EN772

EN772-1 Determination of compressive strength.

The bricks, once their surfaces have been sanded, are placed in a mechanical testing machine. An evenly distributed load is applied until the bricks break.

EN772-3 Determination of net volume and percentage of voids of clay masonry units by hydrostatic weighing.

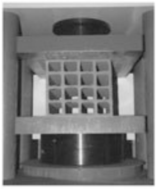
The principle of this test is to obtain the net volume of the masonry units by weighing them in the air and weighing them in water, and subtracting the second result from the total volume, calculated using the brick's dimensions. The volume and percentage of voids of the bricks can also be calculated.

EN772-5 Determination of active soluble salts content of clay masonry units.

The method used involves extracting water from a milled sample, formed of masonry units, and determining the amount of soluble magnesium, and sodium and potassium ions are released during the test. Under certain conditions, these substances can have harmful effects on mortar or on the units themselves.

EN772-7 Determination of water absorption of clay masonry damp proof course units by boiling in water.

The bricks, once dried until reaching constant mass, are weighed and submerged in boiling water for 5 h, then drained and weighed again. A calculation is made of the difference between its dry mass and the increased mass due to saturation.


EN 772-1


EN 772-3


EN 772-5

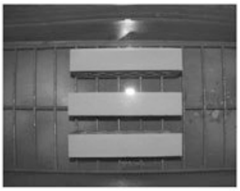

EN 772-7

Table 7.1 EN771-1 requirements [4]

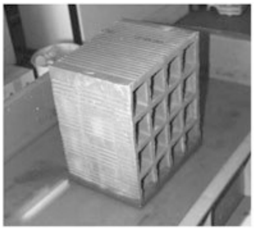
Standard	Title	Characteristic	Tolerance or category
EN772-1 [5]	Determination of compressive strength	Compressive strength and category to be declared by the manufacturer	Category I or II
EN772-3 [6]	Determination of net volume and percentage of voids by hydrostatic weighing		
EN772-5 [7]	Determination of the active soluble salts content	Active soluble salts content to be declared by the manufacturer	S0, S1 or S2
EN772-7 [8]	Determination of water absorption of damp proof course units by boiling in water	Water absorption limits and limits to be declared by the manufacturer	
EN772-11 [9]	Determination of initial rate of water absorption	Initial rate of water absorption limits and limits to be declared by the manufacturer	
EN772-13 [10]	Determination of net and gross dry density	Density to be declared by the manufacturer	D1, D2 or D0
EN772-16 [11]	Determination of dimensions	Average dimensions and limits to be declared by the manufacturer	T1, T2 or T0 R1, R2 or R0
EN772-19 [12]	Determination of moisture expansion of large horizontally perforated clay masonry units	Less than 0.6 mm/m	
EN772-22 [13]	Determination of freeze/thaw resistance	Category to be declared by the manufacturer	F0, F1 or F2
EN1052-3 [14]	Determination of initial shear strength	Mortar bond strength to be declared by the manufacturer	
EN1745 [15]	Methods for determining thermal properties	Thermal properties to be declared by the manufacturer	
EN13501-1 [16]	Fire classification of construction products—Part 1: Classification using test data from reaction to fire tests	Class to be declared by the manufacturer	Class A1 (without need for testing) or other class

Category I: Elements that have compressive strength with confidence level of more than 95 %. Category II: Elements that do not meet the category I confidence requirements

Table 7.2 Classification according to soluble salts content EN772-5 [7]

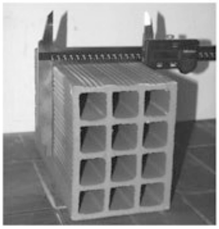
Category	Percentage of mass no greater than	
	Na^+ $+K^+$	Mg^{2+}
S0	Requirements not specified	Requirements not specified
S1	0.17	0.08
S2	0.06	0.03

Tolerance D1: maximum 10 %
Tolerance D2: maximum 5 %
Tolerance D0: deviation by a percentage declared by the manufacturer
Tolerance T1: $\pm 0.4\sqrt{\text{manufacturing size}}$ mm, maximum 3 mm
Tolerance T2: $\pm 0.25\sqrt{\text{manufacturing size}}$ mm, maximum 3 mm
Tolerance T0: deviation in mm declared by the manufacturer
Tolerance R1: $\pm 0\,6\sqrt{\text{manufacturing size}}$ mm
Tolerance R2: $\pm 0\,3\sqrt{\text{manufacturing size},}$ mm
Tolerance R0: limits in mm declared by the manufacturer
Category F0: Passive exposure—masonry or masonry units that are not exposed to humidity or frost
Category F1: Moderate exposure—masonry or masonry units that are exposed to humidity or freeze/thaw cycles
Category F2: Severe exposure—masonry or masonry units that are exposed to water saturation and frequent freeze/thaw cycles due to weather conditions and lack of protection
Class A1: Units that contain organic material, distributed evenly, up to a maximum of 1 % of their mass or volume are classified as A1 fire resistant and do not need to be tested



EN 772-11

EN 772-13



EN 772-16

EN772-11 Determination of water absorption of clay masonry units.

After drying until reaching constant mass, the base surface of the units is submerged in water for a certain period of time and the increase in mass is recorded. The initial rate of water absorption is measured for clay units.

EN772-13 Determination of net and gross dry density of masonry units.

After drying until reaching constant mass, the net and gross volume is calculated, followed by the net and gross dry density of the masonry units.

EN772-16 Determination of dimensions.

After the surfaces have been prepared by removing bumps on the edges that could affect measuring, the length, width and height of the bricks are measured, as well as the width of frogs and hollows, using an appropriate device.

EN772-19 Determination of moisture expansion of large horizontally perforated clay masonry units.

This test measures the difference in the length of bricks caused by submersion in boiling water for 24 h.

EN 772-19

EN 772-22

EN 1052-3

EN772-22 Determination of freeze/thaw resistance of clay masonry units.

A panel of clay masonry units is formed, having been previously immersed in water for a certain period of time. The units are separated using rubber or quick-setting mortar joints that will be sufficiently hard after being immersed in water for a certain period of time. This panel is later cooled, until all the water that has been absorbed is frozen, and the water close to the surface is repeatedly frozen and thawed. The deterioration caused by the freeze/thaw action is assessed and used to determine the bricks' freeze/thaw resistance.

EN1052-3 Determination of initial shear strength.

Masonry's initial shear strength is assessed by the resistance of masonry units that are tested until they are destroyed. The bricks are tested under a four-point load, pre-compressed at right angles to the joints. Four different types of failure must be observed for the results to be considered valid. The initial shear strength is defined by the linear progression curve towards normal zero stress.

7.2.3 CE Marking

The CE marking system proves conformity for products in the European market. Construction products are covered by directive 89/106/EC [17]. Decision 2001/595/EC [18] was published for masonry units, and establishes the system for checking the conformity applicable Fig. 7.3.

European Standard EN771-1 provides for two systems for evaluating conformity: system 2^+ and 4, depending on whether the bricks are classified as category I or category II.

Category I masonry units, as established in EN771-2 (bricks with average mechanical strength whose probability of failure does not exceed 5 %) have been assigned conformity checking system 2^+, which consists of:

- Implementing and maintaining a factory production control system.

Fig. 7.3 CE marking symbol

- Performing initial type testing to check the characteristics of the bricks and regular monitoring tests.
- Performing an initial inspection of the factory and carrying out monitoring inspections to check the production control system, performed by an independent body (notified body).

Category II masonry units (bricks that do not meet the category I confidence levels) have been assigned conformity checking system 4, which consists of:

- Implementing and maintaining a factory production control system.
- Performing initial type testing to check the characteristics of the bricks and regular monitoring tests.

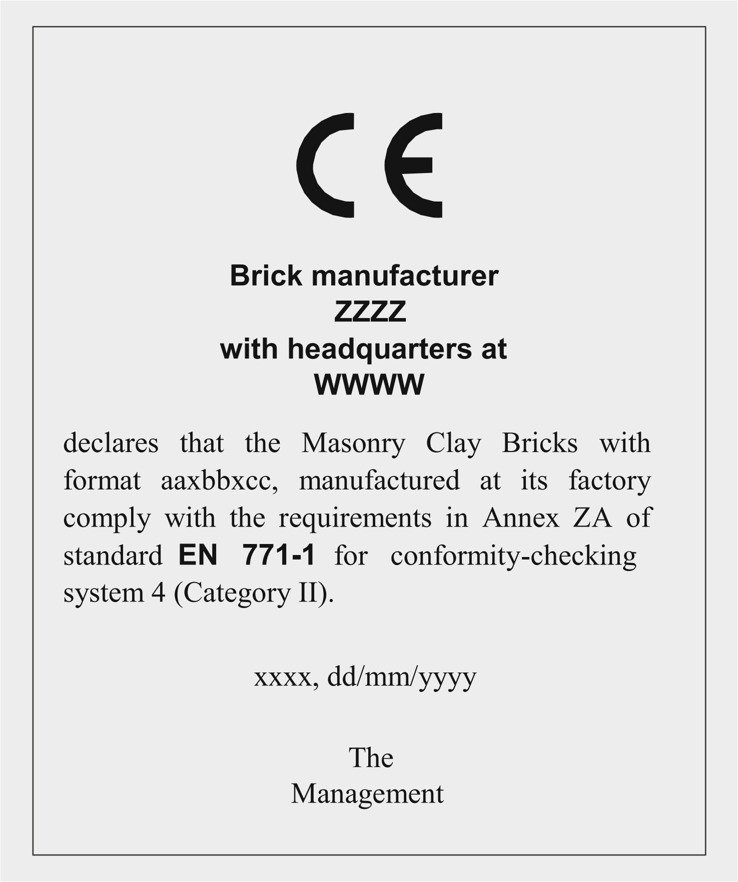
After performing the tasks mentioned above, the manufacturer should mark the product, complete the CE declaration of conformity and issue the CE marking label. Examples of these documents are shown in Figs. 7.4 and 7.5.

7.2.4 Problems with Clay Bricks

7.2.4.1 Action of Sulphates in Mortars and Plasters [1, 4]

Sulphate attack in mortars is mostly caused by the reaction between sulphate in solution and tricalcium aluminate (C3A), found in Portland cement, which forms a calcium sulphoaluminate (ettringite). The risks can be reduced if a sulphate-resisting cement is used. Sulphate attack only occurs if there is a significant quantity of water running through the masonry, either because of seepage or hairline cracks.

The declaration of active soluble salts content established in standard EN771-1 aims to ensure that clay, mortar or plaster units, if used, are not destroyed under particular service conditions. The three categories (S0, S1 and S2) shown on the table specify the maximum soluble salts in water (sodium, potassium and magnesium) for use where different saturation conditions may occur, ranging from situations of prolonged saturation (S2 with common Portland cement in mortar or S1 for sulphate-resisting cement in plastered masonry), normal exposure to atmospheric conditions where masonry is protected with project details (S1) or completely dry areas (S0). Furthermore, soluble sulphates, especially magnesium sulphates, can destroy the clay units themselves, an effect known as



Brick manufacturer
ZZZZ
with headquarters at
WWWW

declares that the Masonry Clay Bricks with format aaxbbxcc, manufactured at its factory comply with the requirements in Annex ZA of standard **EN 771-1** for conformity-checking system 4 (Category II).

xxxx, dd/mm/yyyy

The
Management

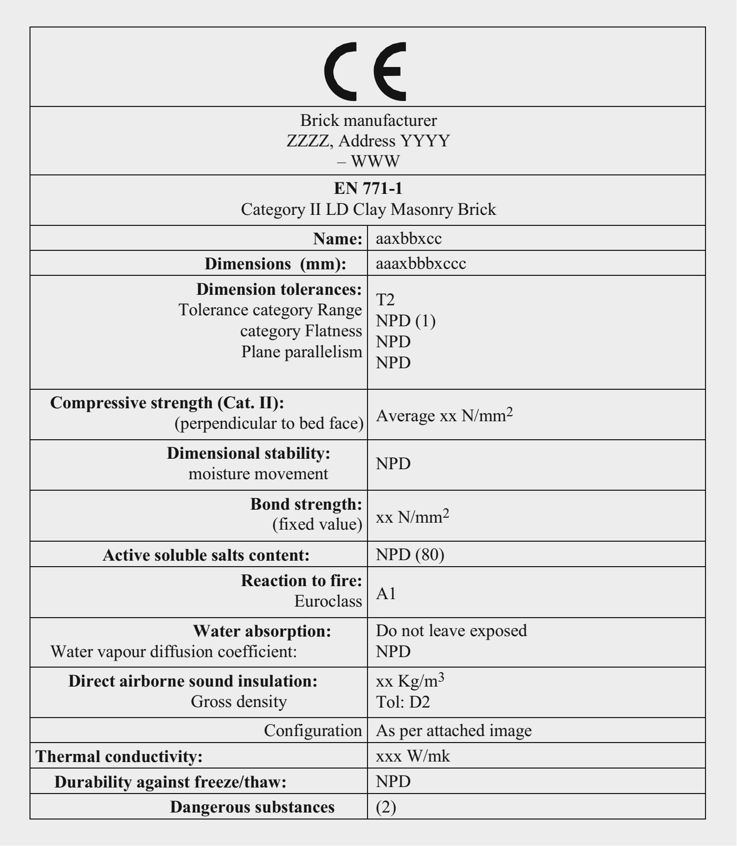
Fig. 7.4 CE declaration of conformity (system 4)

cryptoflorescence, and for this reason separate requirements are given for magnesium.

For fully waterproof masonry, for example, plastered masonry, category S0 is considered appropriate, which means that in such situations it is not necessary to specify requirements for soluble salts.

7.2.4.2 Efflorescence and Stains [4]

The appearance of efflorescence on buildings arises from moisture in the masonry drying. It may be caused by excessive moisture during construction or by inadequate protection, through a lack of project details to protect the masonry from seepage. Furthermore, the soluble material from adjacent mortar or concrete units may increase the number of stains and efflorescence seen in practice.



CE	
Brick manufacturer ZZZZ, Address YYYY – WWW	
EN 771-1 Category II LD Clay Masonry Brick	
Name:	aaxbbxcc
Dimensions (mm):	aaaxbbbxccc
Dimension tolerances: Tolerance category Range category Flatness Plane parallelism	T2 NPD (1) NPD NPD
Compressive strength (Cat. II): (perpendicular to bed face)	Average xx N/mm^2
Dimensional stability: moisture movement	NPD
Bond strength: (fixed value)	xx N/mm^2
Active soluble salts content:	NPD (80)
Reaction to fire: Euroclass	A1
Water absorption: Water vapour diffusion coefficient:	Do not leave exposed NPD
Direct airborne sound insulation: Gross density	xx Kg/m^3 Tol: D2
Configuration	As per attached image
Thermal conductivity:	xxx W/mk
Durability against freeze/thaw:	NPD
Dangerous substances	(2)

Fig. 7.5 CE marking label (system 4)

7.3 Clay Roof Tiles

7.3.1 Manufacturing Process

The manufacturing process for clay roof tiles is very similar to the one used for clay bricks, except for the shaping stage. The process for tiles includes pressing (applicable to most tile models) as well as extrusion, and the firing temperature is slightly higher.

During the shaping stage, large lumps of clay are extruded, which are then pressed to give them the final shape of the roof tile. Unlike bricks, which have their final form after extrusion, roof tiles require (in most cases) pressing to shape them into their final form.

Table 7.3 EN1304 requirements [19]

Standard	Title	Characteristic	Tolerance or category
EN1024 [20]	Determination of geometric characteristics	Evenness, linearity and dimensions	
EN539-1 [21]	Impermeability test	Water impermeability	Category 1 or 2
EN539-2 [22]	Test for frost resistance	Frost resistance (methods A, B, C, D and E). In Portugal, methods C and E are applicable	
EN538 [23]	Determination of flexural strength	Flexural strength declared by the manufacturer	Flat tiles $\geq$600 N
			Flat interlocking tiles $\geq$900 N
			Barrel tiles $\geq$1,000 N
			Other models $\geq$1,200 N
EN13501-1 [16]	Fire classification of construction products—Part 1: Classification using test data from reaction to fire tests	Class declared by the manufacturer	Class A1 (without need for testing) or another class
prEN13501-5 [24]	External fire performance	Class to be declared satisfactory by the manufacturer	Considered

Category 1: (a) test method 1: mean value of impermeability factor $\leq$0.5 cm^3/cm^2/day, and all individual values $\leq$0.6 cm^3/cm^2/day; (b) test method 2: mean value of impermeability coefficient $\leq$0.8, and all individual values $\leq$0.85
Category 2: (a) test method 1: mean value of impermeability factor $\leq$0.8 cm^3/cm^2/day, and all individual values $\leq$0.9 cm^3/cm^2/day; (b) test method 2: mean value of impermeability coefficient $\leq$0.925, and all individual values $\leq$0.95

7.3.2 Regulations Applicable (Specification and Testing)

7.3.2.1 European Standard EN 1304

European Standard EN1304 [19] establishes the specifications to be met by clay roof tiles, as well as the tests applicable. A summary of the EN1304 requirements can be found in Table 7.3.

7.3.2.2 Testing Standards

EN1024 Determination of geometric characteristics.

Measurement of the geometric characteristics of the tiles, specifically the individual dimensions (length and width), surface dimensions, linearity and evenness of form.

EN538 Determination of flexural strength.

The tile is placed on supports and is struck with a load at a speed of 50 N/s until breaking point. The test value is the average of the ten values obtained.

EN539-1 Impermeability (*method 2*).

The tiles are prepared and placed on supports. Water is put in the container. The moment the first drop falls is recorded. The maximum duration of the test is 20 h.

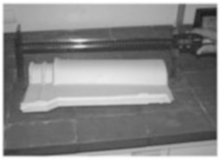
EN539-2 (*method C*).

The tiles are submitted to 50 freeze/thaw cycles in accordance with the standard (−15 and +15 °C). After testing, the loss of mass arising from the test is assessed, as well as any defects caused by the test.

7.3.3 CE Marking

European Standard EN1304, in Annex ZA, establishes that the conformity checking systems applicable for clay tiles are systems 3 or 4, and the choice between the two is made by the manufacturer. Nevertheless, system 3 should be chosen when:

- For legal reasons, the following regulations apply:
  - Reaction to fire performance.
  - External fire performance.


EN 1024


EN 538


EN 539-1


EN 539-2

  - Dangerous substance release.
- Or if the manufacturer decides to perform tests, dispensing their status as “deemed to satisfy” without the need for testing.

Conformity checking system 3 consists of:

- Implementing and maintaining a factory production control system.
- Performing initial type testing to check the characteristics of the tiles by a notified test laboratory, dealing with reaction to fire performance, external fire performance and release of dangerous substances.
- Regular monitoring tests.

Conformity checking system 4 consists of:

- Implementing and maintaining a factory production control system.

Tile manufacturer ZZZZ
with headquarters at WWWW

declares that the Clay Roof Tiles models aaa, bbb, ccc manufactured at its factory comply with the requirements in Annex ZA of standard **EN 1304** for conformity checking system 4.

xxxx, dd/mm/yyyy

The
Management

Fig. 7.6 CE declaration of conformity (system 4)

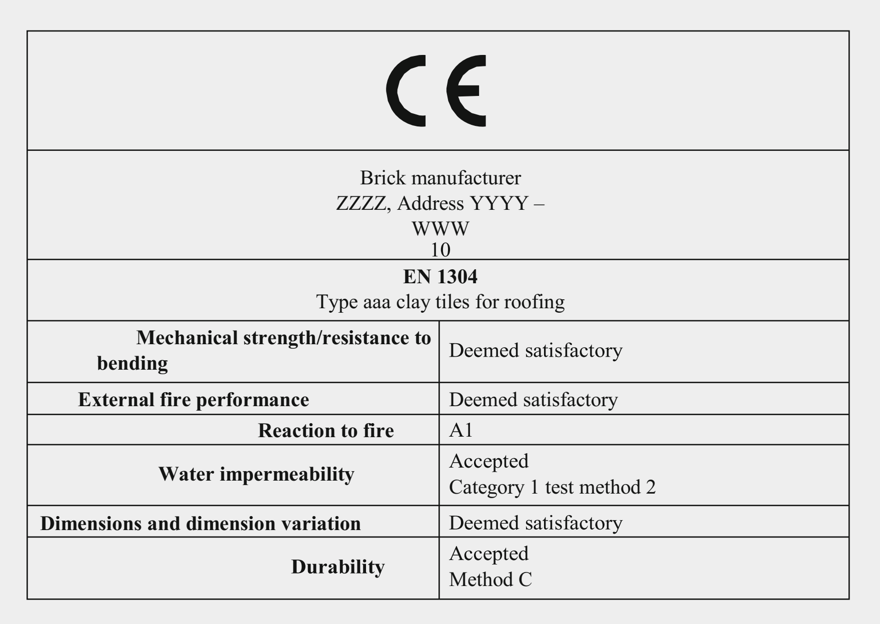
- Performing initial type testing to check the characteristics of the tiles and regular monitoring tests.

After performing the tasks mentioned above, the manufacture should mark the product, complete the CE declaration of conformity and issue the CE marking label. Examples of these documents are shown in Figs. 7.6 and 7.7.

7.3.4 Problems with Clay Roof Tiles

7.3.4.1 Cracks [2]

Even when they have good mechanical strength initially, roof tiles placed on site may undergo significant impacts—causing cracks, splinters and breakages—there may be areas of the roof that do not work as they should. Equipment placed on the



CE

Brick manufacturer
ZZZZ, Address YYYY –
WWW
10

EN 1304
Type aaa clay tiles for roofing

Mechanical strength/resistance to bending	Deemed satisfactory
External fire performance	Deemed satisfactory
Reaction to fire	A1
Water impermeability	Accepted Category 1 test method 2
Dimensions and dimension variation	Deemed satisfactory
Durability	Accepted Method C

Fig. 7.7 CE marking label (system 4)

roofing, hail, heavy objects, tools, moving heavy loads, etc. can all cause breakages and gaps in the material on the visible parts of roof tiles.

The sections where these accidents take place will be weak points, where water seepage is more likely to take place.

7.3.4.2 Accumulation of Moss and Detritus [2]

The functions performed by a roof, which basically aim to keep water out of the building, may be hampered to a great extent, as already mentioned, by an accumulation of detritus, moss, microorganisms and other material on the roof tiles.

When this happens, the roof tiles cannot drain rainwater away easily, and there are often areas where water builds up, leaking into the space underneath the roofing whenever there is enough water or wind to cause it to happen.

7.3.4.3 Peeling Caused by Ice [2]

This is a problem that can occur in roofing even if it uses frost-resistant clay tiles, tested using one of the standardised methods in EN539-2.

The correct use of clay roof tiles should take ventilation (airing) into account, that is, the greater or lesser ability the tiles have to dry out after being saturated by rain or humidity in the air.

If they are not ventilated, they dry slowly. With frequent, prolonged changes in temperature, the roof tile will be liable to freeze/thaw cycles. The volume of the water within the mass of the roof tile fluctuates, which can destroy the clay body if heat and humidity cannot be exchanged with the outside. This is why ventilation is necessary (but not enough) to ensure balance between the air and clay body. The formation of frost is linked to this type of phenomenon.

It is important to note that a roof tile “freezing” will not necessarily cause the tile to peel. The porosity of the tile itself may allow it to cope with an increase in the volume of water in its solid state, acting like a set of compensation chambers. This is an advantage in comparison with other, similar materials.

It is also worth highlighting the ridge of the roof as a critical area, especially those finished with mortar, since mortar has a proportionally worse humidity balance than ceramic material.

By releasing the absorbed water more slowly, the ridge-setting mortar acts as a humidifier, prolonging the time the tiles spend undergoing critical freeze/thaw cycles and, therefore, further reducing their durability.

This problem may also cause the roof tile ribs, battens and frames to come away. The separation of material caused by freeze/thaw cycles almost always lead to problems with the roofing’s efficiency.

7.3.4.4 Variations in Colour [2]

Slight variations in the colour tones of roof tiles are natural and attractive when found together on the same roof. When the roof tiles are fired, there may be normal variations in temperature or in redox atmosphere. As a result, there are variations in colour that are inherent to the manufacturing process.

Provided that the functional qualities of the tiles are not affected, colour specifications do not have any goal other than avoiding detrimental effects for the roofing’s aesthetics. Nevertheless, the action performed by atmospheric agents will lead to slight alterations in colour, although this does not harm the other qualities of the tiles.

7.4 Ceramic Wall and Floor Tiles

7.4.1 Manufacturing Process

Ceramic wall and floor tiles are manufactured from a mixture of several different raw materials, such as clay, kaolin and flux (e.g. sand and feldspar). Floor tiles may have several types of finish: natural, polished or glazed.

The most common manufacturing processes are [3] Figs. 7.8, 7.9 and 7.10:

- Dry pressing
- Extrusion
- Dry
- Semi-wet

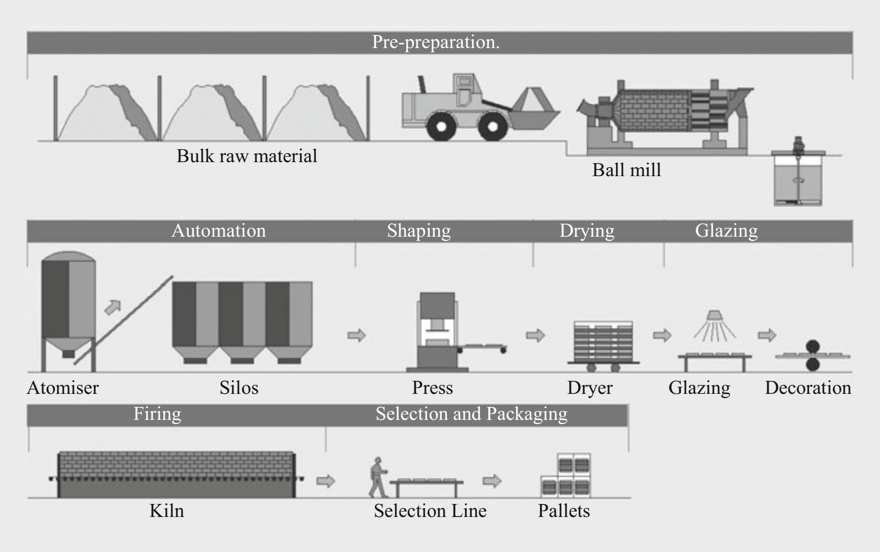


Fig. 7.8 Flow chart of the dry manufacturing process (pressing) [3]

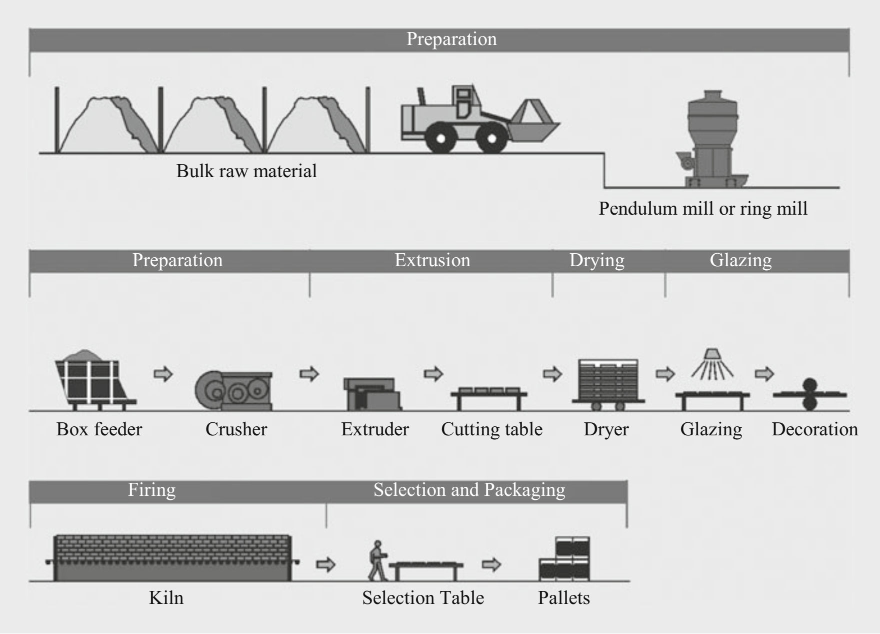


Fig. 7.9 Flow chart of the semi-wet manufacturing process (extrusion) [3]

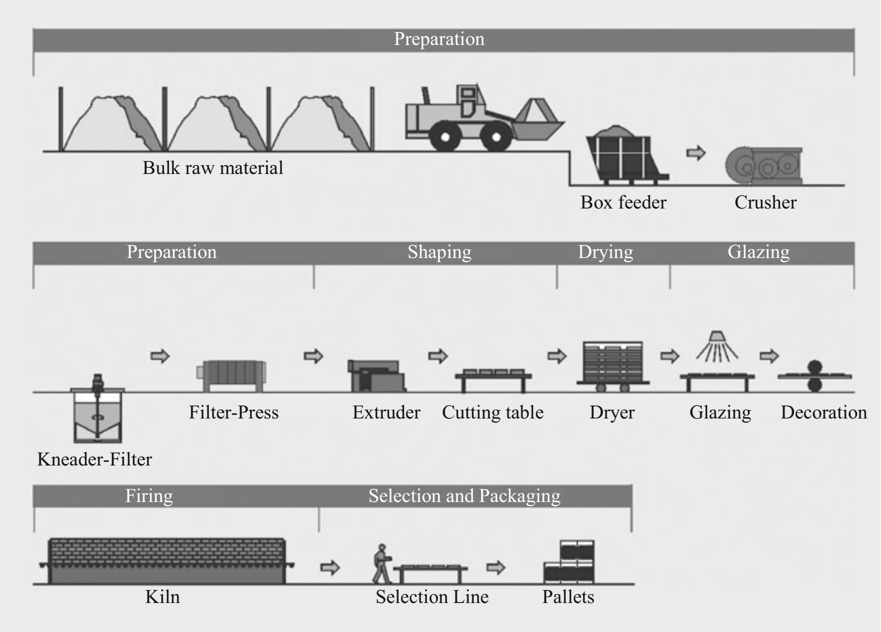


Fig. 7.10 Flow chart of the dry manufacturing process (extrusion) [3]

7.4.1.1 Dry Pressing

The most developed floor tile process is known as single firing, which means that the products are heated (fired) only once. In the double-firing process, the products are fired twice—the first time, just the mixture itself, and the second time for the glaze and decorations.

During the pressing process of the single-firing method, the (hard) flux material is ground in a ball mill, which contains very hard grinding material inside it. The grain size of the material is reduced to the desired size by this process.

The clay is diluted in tanks, sifted and mixed with the milled material; the mixture that is produced is called “barbotine”.

Once the barbotine has been made even, the water is evaporated in atomisers, and the powder produced is stored in silos.

The atomised powder is pressed in hydraulic presses with appropriate dies to obtain the desired dimensions, formats and effects. After pressing, the products move on to dryers, which run at temperatures between 100 and 150 °C, in order to remove the moisture from the shaping stage.

For glazed tiles, the base glaze is applied by special devices (bell, gun, disc, etc.) and the decoration is applied by screen printing, roller printing, etc. After glazing, if there is any, the products are fired at high temperatures, over 1,100 °C, in conveyor tunnel kilns.

After firing, the products are selected from selection lines and, currently, using automatic methods. During this operation, the products are classified in terms of the detection of visual defects (colour, drawing, sand, corners, etc.) or in terms of dimensions.

The tiles are classified in accordance with the type of defects found. Normally, they are divided into first and second selection, in which the first selection does not have visual defects, and the second has small defects that do not hamper their use or performance, under the terms of standard EN14411.

Products may also be separated and classified by calibre. This classification allows the floor tiles to be grouped by size, when dimensions vary slightly from the standard.

If there is any variation in colour (lighter or darker than standard), the products may be classified by batches. Information about the selection, calibre and batch are printed on the packaging.

7.4.1.2 Extrusion (Semi-wet)

The raw materials are prepared in the same way as in the previous processes; the clay, flux and inert materials are mixed together and their grain size is reduced. Water is added to ensure the correct plasticity; the resulting mixture is extruded in extruders so it has the desired dimensions. After extrusion, the material is shaped to the desired length and width, in the same way as in the previous process. Normally, extruded floor and wall ceramics are not decorated, and may be glazed or have a natural finish.

7.4.1.3 Extrusion (Dry)

This process differs from the wet process because water is not introduced during the mixture preparation stage.

The raw materials are mixed together and milled dry, in pendulum or ring mills. The powder is kneaded and dampened, and the resulting mixture is passed through extruders to obtain the desired dimensions.

7.4.2 Regulations Applicable (Specification and Testing)

7.4.2.1 European Standard EN14411

EN14411 [25] introduces term definitions, product classification and criteria for marking ceramic wall and floor tiles, highlighting the following definitions:

Ceramic tiles: thin sheets of clay and/or other non-organic raw materials, generally used for flooring and wall covering and normally shaped by extrusion or pressing at room temperature. They may also be moulded using other processes, and then dried and later fired at temperatures high enough to obtain the required properties; the tiles may be glazed (GL) or unglazed (UGL), are inflammable and are not affected by light.

Extruded tiles (type A): tiles whose mixtures are shaped when plastic, using an extruder. The mixture is then cut into tiles of a predetermined size.

Dry-pressed tiles (type B): tiles formed using a mixture of pre-milled powder, shaped in moulds under high pressure.

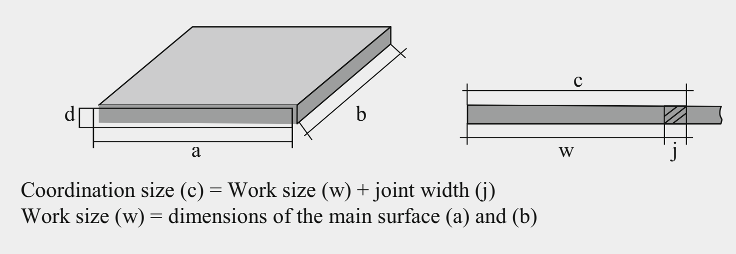


Fig. 7.11 Calculation of tile dimensions [3]

Tiles produced with a different procedure (*C*): tiles manufactured using procedures different from normal commercial methods, that is, extrusion and dry pressing.

Note: *tiles may be produced by moulding*, *when plastic*, *using flat moulds*.

Glazed tiles: tiles that are coated with a waterproof, glazed outer layer.

Note: *these tiles are classified as glazed* (*GL*).

Unglazed tiles: tiles that are not coated with a waterproof, glazed outer layer.

Note: *these tiles are classified as unglazed* (*UGL*).

Engobe tiles: tiles that are given a clay-based coating with a matte finish that may be permeable or impermeable.

Note: *these tiles are classified as unglazed* (*UGL*).

Water absorption (*E*): percentage of mass formed by absorbed water, measured according to EN ISO 10545-3.

Nominal size: dimension used to name the product.

Work size (*W*): dimension of a tile specified for manufacturing, to which the actual size should conform within the permissible tolerance limits Fig. 7.11.

Note: *length*, *width and thickness*.

Actual size: dimensions obtained by measuring the surface of the tile in accordance with EN ISO 10545-2.

Coordination size (*C*): work size plus joint width.

Modular size (*M*): tiles and dimensions based on M, 2M, 3M and 5M modules and also on multiples and subdivisions, with a surface area of less than 9,000 mm^2.

Note: *M* = *100 mm*.

EN 14411 establishes the following criteria for classifying ceramic tiles in groups of products:

Shaping (extrusion or pressing).
Water absorption (E).

The specification standard EN14411 refers to testing standards in the EN ISO 10545 series to determine size and physical and chemical properties Tables 7.4 and 7.5.

Table 7.4 Classification of tiles according to EN14411 [25]

Water absorption Shaping	Group I $E \leq 3$ %		Group IIa $3\ \% < E \leq 6$ %	Group IIb $6\ \% < E \leq 10$ %	Group III $E > 10$ %
A Extruded	Group AI (Annex A)		Group AIIa-1 (Annex B)	Group AIIb-1 (Annex D)	Group AIII (Annex F)
			Group AIIa-2 (Annex C)	Group AIIb-2 (Annex E)	
B Pressed	Group B1a $E \leq 0.5$ % (Annex G)	Group B1b $0.5\ \% < E \leq 3$ % (Annex H)	Group BIIa (Annex J)	Group BIIb (Annex K)	Group BIII (Annex L)
C Other Procedures	Group CI		Group CIIa	Group CIIb	Group CIII

7.4.2.2 Testing Standards (EN ISO 10545)

EN ISO 10545-2—Determination of dimensions: *length and width.*

Tiles with a surface of more than 4 cm^2 are measured using a calliper or other equipment able to make linear measurements. This procedure is used on ten whole tiles, and each side is measured on each tile, more than 5 mm from the corners and approximated to 0.1 mm. An average is taken of the measurements of all sides of the sample to present the final results.

EN ISO 10545-2—Determination of dimensions: *thickness.*

The principle of this test is similar to the previous one, but the equipment used is a micrometre capable of measuring between 5 and 10 mm. An average is taken of the thicknesses of the tiles in the sample to present the final results.

EN ISO 10545-2—Determination of the straightness of sides.

This test is applied to tiles with a surface of more than 4 cm^2. This procedure involves placing the tile with the edge to be measured on two supports placed 5 mm from the corners. After the dial indicator has been set to zero using a calibration plate, the curvature is measured in the middle of the side of the tile, approximated to 0.1 mm. The procedure is repeated for the remaining sides.

EN ISO 10545-2—Determination of Rectangularity.

The tile (surface more than 4 cm^2) is placed with the side to be measured resting on three supports, 5 mm from the corners. After the dial indicator has been set to zero using a calibration plate, the deviation in rectangularity of two adjacent sides is measured 5 mm from the corner of the side and approximated to 0.1 mm. The procedure is repeated for the remaining sides.

Table 7.5 Characteristics required for different uses [3]

	Characteristics	Use	Testing standard
Dimensions and surface quality	Length and width	General	EN ISO 10545-2 [26]
	Thickness	General	EN ISO 10545-2 [26]
	Straightness of sides	General	EN ISO 10545-2 [26]
	Surface flatness (curvature and warpage)	General	EN ISO 10545-2 [26]
	Surface quality	General	EN ISO 10545-2 [26]
Physical properties	Water absorption	Water absorption	EN ISO 10545-3 [27]
	Breaking strength	General	EN ISO 10545-4 [28]
	Modulus of rupture	General	EN ISO 10545-4 [28]
	Resistance to deep abrasion	Unglazed floor tiles	EN ISO 10545-6 [29]
	Resistance to surface abrasion	Glazed floor tiles	EN ISO 10545-7 [30]
	Linear thermal expansion	Locations exposed to heat	EN ISO 10545-8 [31]
	Resistance to thermal shock	Locations exposed to variations in temperature	EN ISO 10545-9 [32]
	Crazing resistance	Glazed tiles	EN ISO 10545-11 [33]
	Frost resistance	External	EN ISO 10545-12 [34]
	Slip resistance	Floor tiles	EN ISO 10545-17 [35]
	Moisture expansion	Locations liable to humidity	EN ISO 10545-10 [36]
	Small colour differences	Tiles of the same colour	EN ISO 10545-16 [37]
	Impact resistance	Floor tiles	EN ISO 10545-5 [38]

(continued)

Table 7.5 (continued)

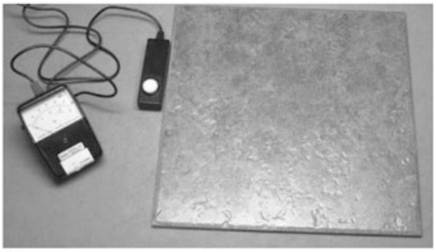
	Characteristics	Use	Testing standard
Chemical properties	Stain resistance	General	EN ISO 10545-14 [39]
	Resistance to acids and alkalis	General	EN ISO 10545-13 [40]
	Resistance to household chemicals and swimming pool salts	General	EN ISO 10545-13 [40]
	Lead and cadmium release	Locations in contact with food	EN ISO 10545-15 [41]

EN ISO 10545-2

EN ISO 10545-2

EN ISO 10545-2—Determination of surface flatness (*curvature and warpage*).

The tile (surface more than 4 cm^2) is placed with the side to be measured resting on three supports, 5 mm from the corners. After the dial indicator has been set to zero using a calibration plate, the deviation in flatness is measured in the middle of the side of the tile, approximated to 0.1 mm. Afterwards, the procedure is repeated for the remaining sides.



EN ISO 10545-2

EN ISO 10545-2—Determination of surface quality.

Before testing begins, the surface quality of the tiles to be tested is assessed. The test specimens are placed so that the observer is 1 m away, measured at right angles from the surface on which they are resting. The surface is illuminated by a bulb with a light intensity of 300 lx in the centre and at the corners.

Standard EN ISO 10545-2 lists the following defects:

- Crack: any fracture in the body of the tile visible on the top surface, back or both.
- Crazing: irregular fissures in the glaze, the same thickness as a hair.
- Dry spots: areas of the surface that do not have glaze.
- Unevenness: unintentional deformation on the tile or glaze.
- Pin holes: Small opening on the surface of a glazed tile.
- Devitrification: unintentional crystallisation on the surface of the glaze.
- Speck or spot: any unintentional mark on the surface of the tile.
- Underglaze fault: any fault in the material covered by glaze.
- Decorating fault: any apparent fault in decoration.
- Chip: fragment removed from a side, corner or surface.
- Blister: small closed cavity in the surface caused by gas being expelled during firing.
- Rough edge: any unintentional unevenness along the edge of the tile.
- Welt: unintentional accumulation of glaze along the edge.

EN ISO 10545-3—Determination of water absorption, apparent porosity, apparent density and actual density.

After the tiles are dried in the drying chamber until they have a constant mass, they are cooled in a desiccator and weighed. Afterwards, the tiles are saturated in boiling water for a certain amount of time and weighed again. They are then weighed once more when submerged.

EN ISO 10545-4—Determination of modulus of rupture and breaking strength.

After drying, once they have constant mass, the tiles are placed on two cylindrical supports, with the main surface facing up. A load is applied to the middle and the breaking load is recorded.

EN ISO 10545-5—Determination of impact resistance by coefficient of restitution.

After the test specimens are placed on the support, a sphere is dropped from a certain height, and the time between the first and second impacts (bounce) of the sphere is recorded.

EN ISO 10545-6—Determination of resistance to deep abrasion of unglazed tiles.

This method consists of determining the resistance of unglazed tiles, measuring the length of the groove created on the surface by a rotating disc under certain conditions and aided by abrasive material.

EN ISO 10545-3

EN ISO 10545-4

EN ISO 10545-5

EN ISO 10545-6

EN ISO 10545-6—Determination of resistance to surface abrasion of glazed tiles.

The method used to determine glazed tiles' resistance to surface abrasion consists of a rotating abrasive load being applied to the surface of the tile and making a visual comparison between the specimens tested and specimens not tested.

Stage of abrasion; visible mark to number of rotations	Class
100	0
150	1
600	2
750, 1,500	3
2,100, 6,000, 12,000	4
>12,000[a]	5

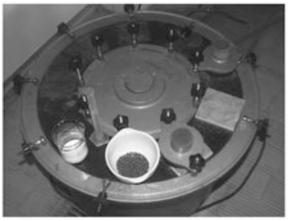
[a] Should pass the test for stain resistance, in accordance with standard EN ISO 10545-14.

EN ISO 10545-8—Determination of linear thermal expansion.

Determination of the linear thermal expansion coefficient at a temperature range between room temperature and 100 °C.

EN ISO 10545-9—Determination of resistance to thermal shock.

This test aims to determine resistance to thermal shock in whole tiles between 15 °C (water or abrasive) and 145 °C (drying chamber). For tiles with water absorption of 10 % or lower, the tiles are immersed vertically in water between 15 ± 5 °C.



EN ISO 10545-7

EN ISO 10545-8

EN ISO 10545-9

For tiles with water absorption of more than 10 %, the tiles are placed with the glazed side in contact with aluminium abrasive on water at 15 ± 5 °C.

After staying at a lower temperature, the tiles are placed in the drying chamber at a temperature of 145 ± 5 °C until the temperature becomes uniform and they are then placed once again in the low temperature water (cycle repeated ten times).

EN ISO 10545-10—Determination of moisture expansion.

Moisture expansion is determined by subjecting the re-fired tiles to boiling water and measuring the subsequent change in size.

After the first re-firing, the specimens are measured and subjected to heat treatment (boiling water) for 24 h and then measured again.

EN ISO 10545-11—Determination of crazing resistance of glazed tiles.

The tiles are placed in an autoclave and subjected to 5 bar pressure for 2 h. The glazing is checked for crazing.

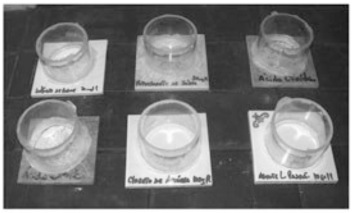
EN ISO 10545-12—Determination of frost resistance.

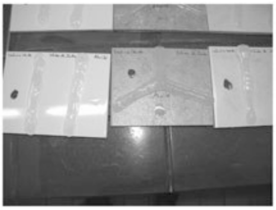
After drying, once at constant mass, the tiles are weighed and saturated with water, then weighed again. Later, they are placed in a refrigeration room, where they undergo 100 freeze/thaw cycles (−5°C and +15 °C). At the end, they are weighed and checked for any defects that may have appeared.


EN ISO 10545-10


EN ISO 10545-11


EN ISO 10545-12


EN ISO 10545-13


EN ISO 10545-14


EN ISO 10545-16

EN ISO 10545-12—Determination of chemical resistance.

Testing solutions are allowed to act on the specimens, and the effects of the attack are visually assessed after a certain amount of time.

EN ISO 10545-12—Determination of stain resistance.

The surface of the specimens is kept in context with testing solutions, and the materials in contact with the surface of the tiles for a certain period of time. The surfaces then undergo specific cleaning methods and are finally inspected to check for any alterations.

EN ISO 10545-15—Determination of lead and cadmium release from glazed tiles.

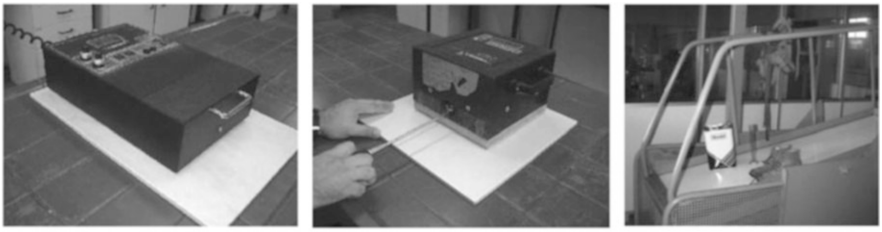
The glazed surface of the tiles is exposed to an acetic acid solution, and afterwards the amount of lead and cadmium released to the solution is determined using an appropriate method.

EN ISO 10545-16—Determination of small colour differences.

Comparison between the CMC[1] (DECMC)[2] colour of the sample and a reference value, using a factor agreed upon beforehand (cf)[3].

EN ISO 10545-17—Determination of slip resistance.

The kinetic coefficient of friction is measured using a slider, moving at constant speed over a horizontal surface (method A).



EN ISO 10545-17

The static coefficient of friction is determined by measuring the force needed to move the slider from rest, on a horizontal surface (method B).

The kinetic critical angle is measured using a lubricated, sloped platform. This slope increases gradually, while somebody walks over it (method C).

7.4.3 CE Marking

European Standard EN14411, in Annex ZA, establishes that the conformity checking systems applicable for ceramic tiles are systems 3 or 4. System 3 should be chosen for coverings designed to come into contact with food and whenever there are regulations approved for the release of dangerous substances.

Conformity checking system 3 consists of:

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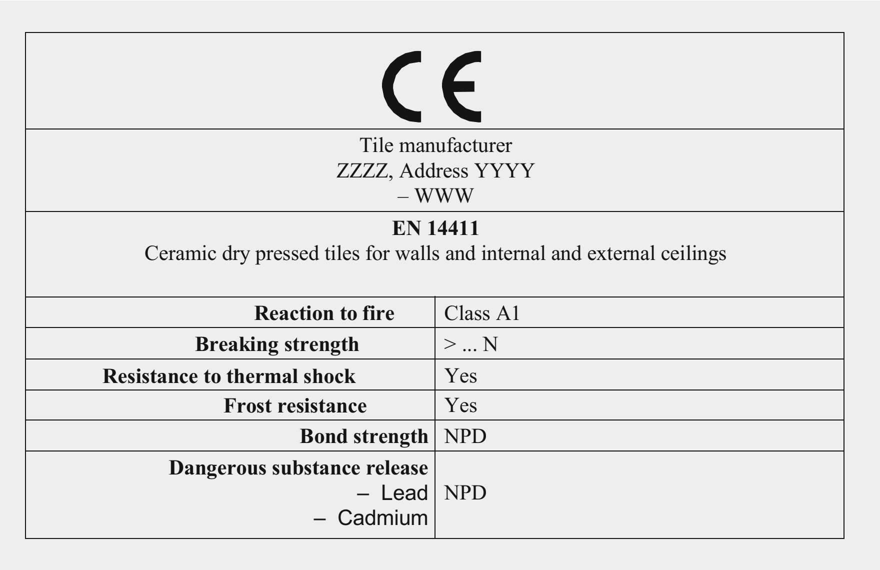
[1] Colour Measurement Committee.

[2] CIELAB L*C*h method derived from the CIE L*a*b method.

[3] For the ceramics industry, 0.75 is an acceptable value.



CE

Tile manufacturer
ZZZZ, Address YYYY
– WWW

EN 14411
Ceramic dry pressed tiles for walls and internal and external ceilings

Reaction to fire	Class A1
Breaking strength	> ... N
Resistance to thermal shock	Yes
Frost resistance	Yes
Bond strength	NPD
Dangerous substance release – Lead – Cadmium	NPD

Fig. 7.12 CE marking label (system 4)—covering

- Implementing and maintaining a factory production control system.
- Performing initial type testing for tiles in a notified laboratory regarding the release of dangerous substances, specifically lead and cadmium.
- Regular monitoring tests.

Conformity checking system 4 consists of:

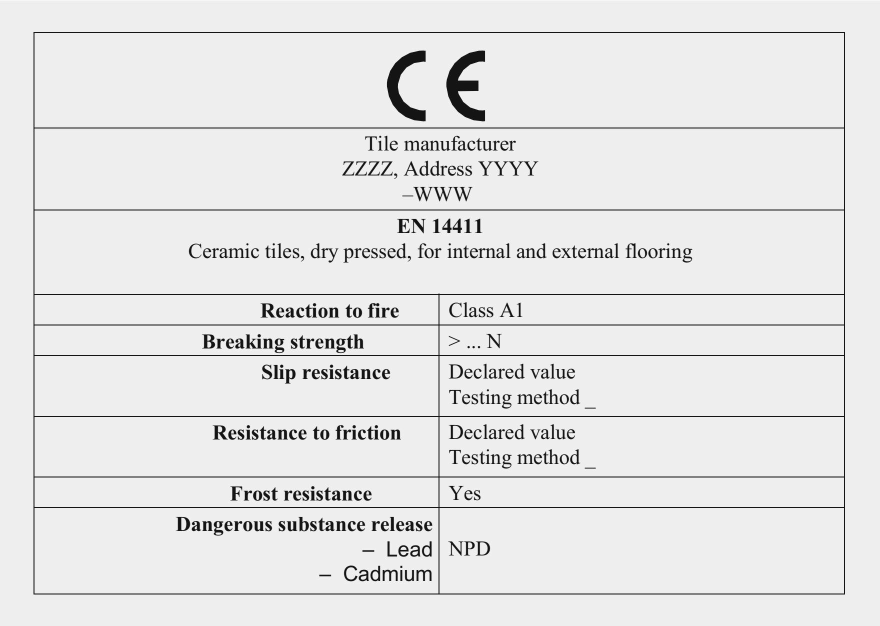
- Implementing and maintaining a factory production control system.
- Performing initial type testing to check the characteristics of the ceramic tiles and regular monitoring tests.

After performing the tasks mentioned above, the manufacturer should mark the product, complete the CE declaration of conformity and issue the CE marking label. Examples of the labels for wall and floor tiles are shown in Figs. 7.12 and 7.13, respectively.

7.4.4 Problems with Ceramic Tiles

The main problems associated with ceramic tiles are:

- Mechanical deterioration.
- Breaking.
- Chemical deterioration.



CE

Tile manufacturer
ZZZZ, Address YYYY
–WWW

EN 14411
Ceramic tiles, dry pressed, for internal and external flooring

Reaction to fire	Class A1
Breaking strength	> ... N
Slip resistance	Declared value Testing method _
Resistance to friction	Declared value Testing method _
Frost resistance	Yes
Dangerous substance release – Lead – Cadmium	NPD

Fig. 7.13 CE marking label (system 4)—flooring

- Surface defects (dry spots, bumps and blisters).
- Crazing and cracks.
- Efflorescence.
- Deterioration due to frost.

The problems arising in ceramic tiles may often be associated with how they are installed, since they often appear only after use.

Mechanical deterioration. This problem could be linked not only to an intrinsic “defect” of ceramic tiles, but is often related to a poor choice of tile for the place where it is installed “worn” tiles often found around the counter at cafés.

Breaks. Ceramic materials are mechanically fragile and are not very resilient, so when they undergo impacts they tend to break. When choosing a ceramic tile for use in areas with a high risk of impact, tile thickness and impact resistance, among other characteristics, should be taken into account.

Chemical deterioration. The chemical deterioration of ceramic tiles has been evaluated and is well known. Nevertheless, flooring and covering often undergo maintenance treatments that are not appropriate for their chemical properties. Ceramic tiles may also be inappropriate for the place where they are installed.

Surface defects. Often, these “defects” are already found in the ceramic tiles, but when they are installed they appear intensely enough for them to be considered a problem. This is clearly a problem linked with tiles.

Crazing and cracks. As in the previous case, this is a problem that use helps to reveal. They are defects that are not visible to the naked eye, but when installed grow and become a problem and affect the aesthetics and usage of the flooring/covering.

Efflorescence. This problem is revealed by the appearance of "stains" or "dust" on the surface of the tiles or next to the joints. Normally, it is caused by two situations:

- Composition of the tiles (existence of soluble salts in the mixture, which dissolve in the presence of water and rise to the surface).
- Interaction between the ceramic and the base on which it is laid.

Deterioration due to frost. Deterioration due to frost occurs through peeling on the surface of tiles. As well as the intrinsic characteristics of ceramic, the conditions where they are installed should also be considered (laying mortar, joints, etc.). During the "freezing" period, water increases in volume, which may lead to cracks in the material and subsequent peeling if the microstructure of the ceramic is not adequate. The consequences of this problem may affect usage as well as aesthetics.

7.5 Recovery of Ceramic Waste

The waste produced by the ceramics industry is normally known as potsherd and its recovery is still not particularly efficient. However many ceramic industries now recycle their potsherd during the process itself or supply it to other types of industry.

The incorporation of "potsherd" into the composition of ceramic product mixtures is evolving so that it can be recovered. This means that the amount of natural raw materials can be reduced, helping to improve environmental sustainability, since they are becoming scarcer and scarcer resources.

On the other hand, energy use is also helped by incorporating potsherd into the ceramic mixture, reducing the energy bill and helping improve the factory's environmental sustainability—reduction in CO_2 emissions.

Often, it is believed that the ceramics industry can neutralise the waste from other industries, particularly waste that is considered dangerous.

Waste from the ceramics industry (potsherd) has a wide variety of recovery options and creates sustained improvements for the products in which it is incorporated. Examples of incorporation include addition to concrete, mortars and ceramics themselves (often another type of product). Many of these possible uses are being researched with positive results, encouraging waste to be recovered in order to improve the characteristics of the products that incorporate it.

Sustainable development "obliges" us to act to sensibly recover waste everywhere, and particularly in the ceramics industry, in order to progressively stop using landfills and to recycle waste and produce the subsequent advantages for the environment.

References

1. Manual de Alvenaria de Tijolo (2009) APICER/CTCV, 2^{a} ed. Coimbra
2. Manual de Aplicação de Telhas Cerâmicas (1998) APICER/CTCV, 1^{a} ed. Coimbra
3. Manual de Aplicação de Revestimentos Cerâmicos (2003) APICER/CTCV, $1.^{a}$ ed. Coimbra
4. EN771-1:2003 Specification for masonry units—part 1: clay masonry units. CEN, Brussels
5. EN772-1:2000 Methods of test for masonry units—part 1: determination of compressive strength. CEN, Brussels
6. EN772-3:1998 Methods of test for masonry units—part 3: determination of net volume and percentage of voids of clay masonry units by hydrostatic weighing. CEN, Brussels
7. EN772-5:2001 Methods of test for masonry units—part 5: determination of active soluble salts content of clay masonry units. CEN, Brussels
8. EN772-5:1998 Methods of test for masonry units—part 7: determination water absorption of clay masonry damp proof course units by boiling in water. CEN, Brussels
9. EN772-11:2000 Methods of test for masonry units—part 11: determination of water absorption of aggregate concrete, autoclaved aerated concrete, manufactured stone and natural stone masonry units due to capillary action and the initial rate of water absorption of clay masonry units. CEN, Brussels
10. EN772-13:2000 Methods of test for masonry units—part 13: determination of net and gross dry density of masonry units (except for Natural Stones). CEN, Brussels.
11. EN772-16:2000 Methods of test for masonry units—part 16: determination of dimensions. CEN, Brussels
12. EN772-19:2000 Methods of test for masonry units—part 19: determination of moisture expansion of large horizontally perforated clay masonry units. CEN, Brussels
13. EN772-22:2006 Methods of test for masonry units—part 22 determination of freeze/thaw resistance of clay masonry units. CEN, Brussels
14. EN1052-3:2002 Methods of test for masonry—part 3 determination of initial shear strength. CEN, Brussels
15. EN1745:1999 Masonry and masonry products—methods for determining declared and design thermal values, CEN, Brussels
16. EN13501-1:2007 Fire classification of construction products and building elements—part 1: classification using test data from reaction to fire tests. CEN, Brussels
17. Directive 89/106/EC Construction products of 21 December 1989. O.J. no. L40/12 of 12.02.89
18. Decision 2001/596/EC Masonry Products O.J. no. L 209/33 of 02.08.2001
19. EN1304:1998—Clay roofing tiles for discontinuous laying. Product definitions and specifications. CEN, Brussels
20. EN1024:1997—Clay roofing tiles for discontinuous laying. Determination of geometric characteristics. CEN, Brussels
21. EN539-1:2005—Clay roofing tiles for discontinuous laying. Determination of physical characteristics. Part 1: Impermeability test, CEN, Brussels
22. EN539-2:2006—Clay roofing tiles for discontinuous laying. Determination of physical characteristics. Part 2: Test for frost resistance. CEN, Brussels
23. EN538:1994—Clay roofing tiles for discontinuous laying. Flexural strength test. CEN, Brussels
24. EN13501-5:2005 Fire Classification of construction products and building elements—part 1: classification using data from external fire exposure to roofs tests. CEN, Brussels.
25. EN14411:2006—Ceramic tiles—definitions, classification, characteristics and marking. CEN, Brussels
26. EN ISO 10545-2:1995—Ceramic tiles—part 2: determination of dimensions and surface quality. CEN, Brussels
27. EN ISO 10545-3:1995—Ceramic tiles—part 3: determination of water absorption, apparent porosity, apparent relative density and bulk density. CEN, Brussels

28. EN ISO 10545-4:1995—Ceramic tiles—part 4: determination of modulus of rupture. CEN, Brussels
29. EN ISO 10545-6:1995—Ceramic tiles—part 6: determination of resistance to deep abrasion for unglazed tiles. CEN, Brussels
30. EN ISO 10545-7:1996—Ceramic tiles—part 7: determination of resistance to surface abrasion for glazed tiles. CEN, Brussels
31. EN ISO 10545-8:1994—Ceramic tiles—part 8: determination of linear thermal expansion. CEN, Brussels
32. EN ISO 10545-9:1994—Ceramic tiles—part 9: determination of resistance to thermal shock. CEN, Brussels
33. EN ISO 10545-11:1994—Ceramic tiles—part 11: determination of crazing resistance for glazed tiles. CEN, Brussels
34. EN ISO 10545-12:1995—Ceramic tiles—part 11: determination of frost resistance. CEN, Brussels
35. EN ISO 10545-17:1995—Ceramic tiles—part 17: determination of coefficient of friction
36. EN ISO 10545-10:1995—Ceramic tiles—part 10: determination of moisture expansion. CEN, Brussels
37. EN ISO 10545-16:1999—Ceramic tiles—part 16: determination of small colour differences. CEN, Brussels
38. EN ISO 10545-5:1996—Ceramic tiles—part 5: determination of impact resistance by measurement of coefficient of restitution. CEN, Brussels
39. EN ISO 10545-14:1995—Ceramic tiles—part 14: determination of resistance to stains. CEN, Brussels
40. EN ISO 10545-13:1995—Ceramic tiles—part 13: determination of chemical resistance, CEN, Brussels
41. EN ISO 10545-15:1995—Ceramic tiles—part 15: determination of lead and cadmium given off by glazed tiles. CEN, Brussels

Glass

8

M. Clara Gonçalves

FORTUNA VITREA EST: TUM CUM SPLENDET, FRANGITUR

Abstract

In architecture, glass established itself as an element that provided cohesion between the inside and the outside. Glass is a transparent structural material and one of the few building materials that combines tradition with technological innovation. Glass is a product that harmonises colour, reflectance, transparency or opacity, texture and thickness, flatness or curvature with, for example, some control over opacity or self-cleaning properties, whilst at the same time being low-emissive, heat and/or sound insulator, offers protection and security, as well as resistance to thermal shock and impact from projectiles. Moreover glass is the only material that is 100 % recyclable, what we should bear in mind, as sustainable development is only possible by careful use of resources and technology. Glass is, definitively, a hard product to beat.

Keywords

Float, ordinary-glass • Decorated-glass • Silkscreen-printed glass • Rolled-plate-glass • Coated-glass • Anti-reflection-glass • Mirror-glass • Low-emissivity-glass • Self-cleaning-glass • Safety-glass • Laminated-glass • Tempered-glass • Fire-retarding glass • Double-glazing-glass

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M.C. Gonçalves, F. Margarido (eds.), *Materials for Construction and Civil Engineering*, DOI 10.1007/978-3-319-08236-3_8

8.1 Glass in Construction and Architecture: Brief History

Glass is a material that was manufactured 5,000 years ago (*hollow glass*) and first used in houses at least 2,000 years ago (*flat glass*). Today it has a significant role in building construction, particularly in lightweight *façades,* where increasingly light structures are constantly being developed and applied. The choice of thickness and type of glass to use is up to the architect and materials engineer.

But glass was used even before it was manufactured. Some of the natural phenomena that produced glass include the melting of magma and meteorite impacts, followed by rapid cooling. Natural glass is structurally disordered; it is very tough, with *shell-like* fracture, very shiny, translucent or transparent, with many different colours, from grey to dark brown, red to green, and irisation due to colloidal dispersion of metallic impurities. Natural glass was used for millennia as a raw material to produce works of art along with functional objects, such as the point of a lance or as arrow tips, where it competes with silex (Fig. 8.1). Of all natural glass, obsidian was the most used due to its relative abundance.

Associated with high temperature manufacturies—such as ceramics and metallurgy—glass production would have emerged accidentally; melting copper minerals can cause opaque and blue-tinted vitreous slag to form, and heating the ceramic pieces can cause them to vitrify. The first manufactured glass would have been used as a *coating* (*glaze*) for ceramic or metal pieces and natural rock.

Fig. 8.1 Obsidian chips and arrow tips, IV and VI centuries, Mexico (Courtesy of Museu Arqueológico do Carmo, Lisboa, Portugal)

The oldest known glass *glaze* (dating from 12,000 BC) comes from Ancient Egypt. The fired ceramic pieces were dipped in a slurry made of sand (rich in quartz) and sodium salts (carbonates, bicarbonates, sulphates, chlorides or plant ash) and submitted to a second fired, forming a glaze.

Over time, various types of glaze were developed. Opaque and coloured glazes in many shades were developed using tin; the Ishtar Gate (Babylon, seventh century BC) is one stunning example. Lead-rich glaze, with a low melting point, emerged in China (during the Han dynasty, 206–200 BC).

But the *democratisation* of glass pieces developed much later. The temperature needed to melt the raw materials would definitely have been one of the main obstacles. The oldest known hollow glass object (a dark blue Egyptian amulet dating from 7,000 BC) has a high level of copper oxide, supporting the hypothesis that metal-based slag was remelted. The Egyptians developed a new moulding glass concept which replaced the earlier methods and improved the quality of the glassware. New glass products reasonably transparent, although usually still filled with bubbles and other flaws, were produced. The bottles and pots were formed by winding glass ribbons around a mould of compacted sand. After cooling the glass, the sand was scraped from inside the bottle, leaving a hollow container with rough, translucent walls and usually lopsided shapes (Fig. 8.2).

Fig. 8.2 Oriental Mediterraneo glasses produced with Egyptian technique (internal sand mould): (**a**) amphoriskos, I–II century, and (**b**) alabastron, V century (Courtesy of Museu da Farmácia, Lisboa, Portugal)

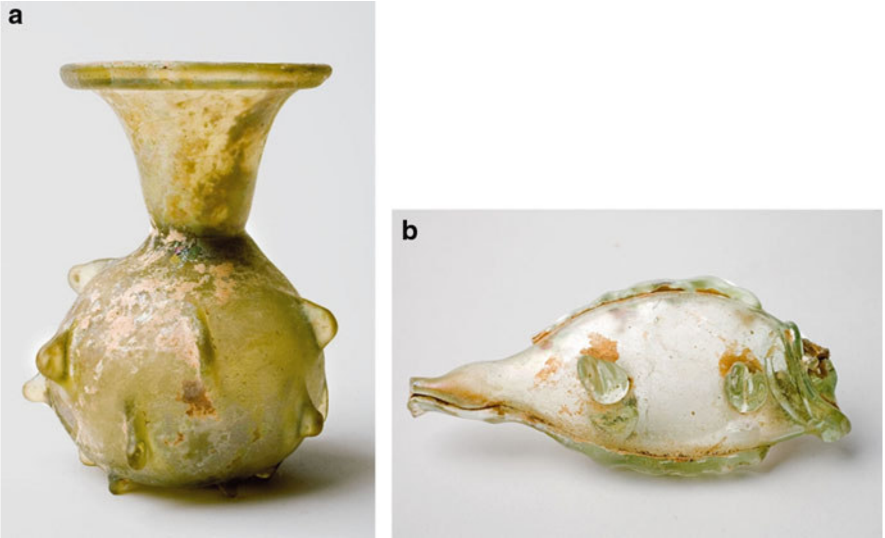


Fig. 8.3 Oriental Mediterraneo blown glasses: (**a**) sprinkler bottle, V century, and (**b**) fish bottle, III–IV century (Courtesy of Museu da Farmácia, Lisboa, Portugal)

In Mesopotamia (3,000 BC), along with the large-scale production of (hollow) glass pieces, a glass protocol was written. From 2,000 BC to 1,000 BC, the glass-producing centre spread to Syria, Greece and Italy. In 200 BC, in the city of Babylon, the first industrial revolution in glass manufacturing takes place—glass-blowing, where glass is blown using a blow tube. The quality of glass-blowing improved dramatically and glass drinking vessels became popular. Coloured glasses came into common use, with techniques for production of many colours regarded as family secrets, to be passed on from generation to generation of artisans (Fig. 8.3).

The Syrian glass-blowing technique and the Alexandrian art of *millefiori* were quickly adopted by the Romans. But the splendour of the arts in Rome also included flat glass (Fig. 8.4). Flat glass was used to build *high standard* buildings, for floors and wall decorations, but it was its use for windows (where it replaced mica and shells) where it contributed most to Architecture. In the ruined cities of *Pompeii* and *Herculaneum*, there are numerous traces of sheets of glass probably used in the windows of the public baths. The fall of Imperial Rome and the instability caused by the Huns in mediaeval Europe caused the glass-producing centres to decline.

During the European Middle Ages, small glass-making centres were established hidden in forests (Fig. 8.5). The combination of the discovery of many new colourants with the invention of glass-blowing eventually led to the magnificent stained glass windows of so many of the great cathedrals of Europe and the Near East (Fig. 8.6).

In the eighth century, the revival of trade with the Byzantine Empire led to renewed glass production in Europe. Venice became the most prestigious glass-

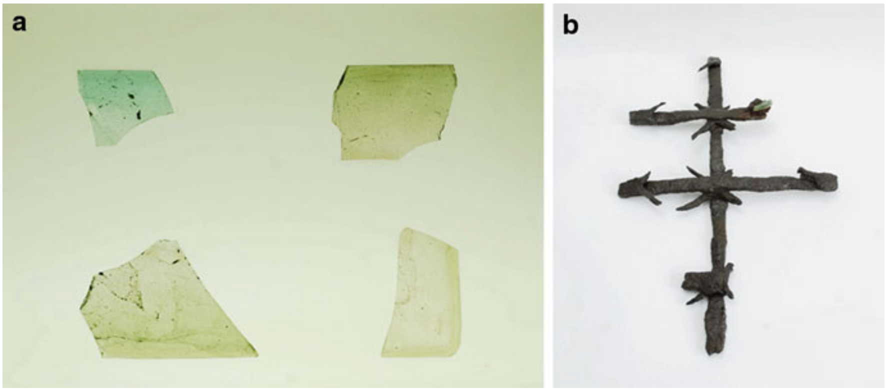


Fig. 8.4 Roman flat glass in Conímbriga: (**a**) pieces of window glass and (**b**) window frame, where a piece of glass can still be seen (Courtesy of Museu de Conímbriga, Portugal)

Fig. 8.5 During the European Middle Ages, small glass-making centres were established hidden in forests (British Library, Londres)

Fig. 8.6 Our Lady of Rosário, sixteenth century stained glass from chancel of Mosteiro da Batalha, Portugal (Courtesy of Dr. Pedro Redol, Director of Mosteiro da Batalha, Portugal)

producing centre, which kept various manufacturing methods and techniques secret for centuries. Under the pretext of protecting Venice from fire, Venetian artisans were forced to reinstall their kilns in Murano, where they would remain prisoners of their art and ingenuity.

For five millennia, various glass objects were manufactured, initially as containers and mainly for holding food, oils and perfumes or simply for decorative purposes. Initially, Roman architecture and then the monumentality of mediaeval and Gothic religious art had a great artistic influence on flat glass. However, the manufacturing process for producing flat glass constantly faced big problems. It was only with the dawn of the Industrial Revolution that sheets of glass could be produced that were large enough to allow more extensive use in architecture and throughout society in general. With glass, more than with any other material, art and technology have been merged in an exceptional way for millennia.

8.2 Glass Composition and Structure

8.2.1 What Is Glass?

Although most solid materials are crystalline (or partly crystalline), some materials do not organise their atoms within a 3D periodic network. Thermoplastics, transparent polymers, rubbers, oxide glass, fluoride, chalcogenides and also metallic glass are some examples.

A glass can be defined as an amorphous solid completely lacking in long-range, periodic atomic structure and exhibiting a region of glass transformation behaviour. Any material, inorganic, organic or metallic, formed by any technique, which exhibits glass transformation behaviour, is a glass.

Most commercially available glasses are prepared by traditional melting and quenching processes, whilst preventing crystallisation, with the melt structure becoming *frozen* below T_g. Crystallisation and glass formation are commonly discussed on the basis of either enthalpy or volume *versus* temperature diagrams, such as that shown in Fig. 8.7. Since enthalpy and volume behave in a similar fashion, the choice of one of them is quite similar. As we cool the liquid, its atomic structure continuously changes depending on the temperature of the liquid. Cooling to any temperature below the melting temperature (T_M) of the system would commonly result in the formation of a crystalline solid, where the atoms, molecules or ions arrange themselves to create a solid with long-range, periodic arrangement. When this occurs, the enthalpy/volume shows a discontinuous decrease relative to the enthalpy of the liquid. Continued cooling of the crystal will result in a further decrease in enthalpy due to the heat capacity of the crystal. All the materials tend to crystallise at T_M. However, crystal formation is not instantaneous but occurs over time as molecular and/or ionic restructuring takes place, through diffusion.

When the liquid is cooled below T_M of the system without crystallisation, a supercooled liquid is obtained (Fig. 8.7). As the temperature decreases, the structure of the liquid continues to rearrange, but no discontinuity in the enthalpy curve

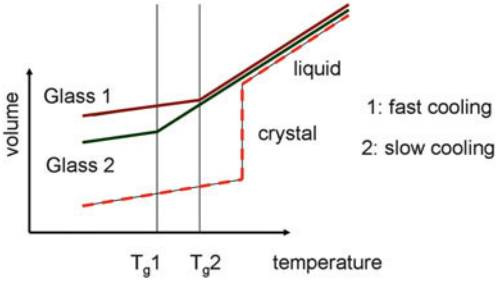


Fig. 8.7 Volume *versus* temperature diagram

is observed. Whilst the liquid cools, the viscosity increases, atomic and molecular movements slow down, and a point may be reached where the liquid structure becomes ‘frozen’ and no longer depends on temperature. Meanwhile, the enthalpy line deviates from the equilibrium enthalpy curve by decreasing its slope. The temperature range limited by the temperature of the last liquid in equilibrium and that of the first ‘frozen’ solid is known as the glass transformation region. Since the temperature where the enthalpy starts diverging from the equilibrium curve is controlled by the liquid viscosity, a lower cooling rate will shift the glass transformation region to a lower temperature range.

Glass Formation

When a liquid cools, its specific volume decreases (Fig. 8.7). When it cools slowly, the liquid crystallises at melting temperature, T_M. At this temperature, there is a drastic reduction in volume, due to smaller average spacing between the atoms/ions.

All materials tend to crystallise at T_M as this is the lowest free energy state of the system.

The crystallisation process is not instant but occurs over a period of time in which atomic/ionic/molecular diffusion takes place forming a crystal network.

For many materials, it is possible to suppress crystallisation by rapidly cooling the melt.

Any amorphous (or glassy) material is defined by a key temperature—the temperature of glass transition (T_g). T_g marks the limit between which the amorphous material is in a rigid state ($T < T_g$) and where it demonstrates plastic behaviour.

Glass Transition Temperature

The temperature of glass transition (T_g) is a set temperature which separates the point at which an amorphous material has a rigid state and when it demonstrates plastic behaviour.

At temperatures below T_g, where it is in a brittle state, the amorphous materials are called glass. In this temperature range, the glass is structurally rigid and thus unable to absorb mechanical energy.

Between the glass and liquid state, amorphous materials are essentially supercooled liquids. In this temperature range, the molecules can move around, causing the amorphous material to become plastic.

If glass is left around a glass transition temperature for a long enough time period, the likelihood of devitrification increases, although this is not a problem in the modern glass-making process.

Modern theories of glass formation no longer address the question of why a specific material will form a glass, but rather how fast it needs to be cooled from melting to allow glass formation. In theory, any material can be turned into glass, provided that the cooling down of its molten state is fast enough to enable the atomic/ionic diffusion required to form crystals. The term crystallisation actually refers to a combination of two processes—nucleation and crystal growth. Crystallisation requires the presence of a nucleus on which the crystal will subsequently grow to a detectable size. The nucleus may be either homogeneously formed, through a driving force for solidification when a liquid is cooled below T_M, or heterogeneously formed at a pre-existing surface, such as the surface of an impurity, a nucleating agent (a deliberately added nano-/microcrystal), crucible walls, etc. Homogeneous nucleating systems are uncommon, and the majority of crystallisation is heterogeneous.

If no nuclei are present, crystal growth cannot occur and the material will form a glass. When some nuclei are present but no growth has occurred, the extremely small size and low volume fraction of the nuclei prevents their detection, so the solid is, for all practical purposes, still a glass. Even if long-range order is lacking, some crystalline clusters or *ordered domains* extending beyond nearest neighbours to the subnanometre scale may be present. These small *clusters* can act as seeds for crystallisation and, therefore, affect the final structure and final properties of the glassy material.

Properties of Glass Made from Oxides

- Transparency
- Smooth and shiny surface
- Less dense than crystal with an identical chemical composition
- Temperature of glass transition (T_g)
- High chemical stability (except for fused silica or silica that has been modified using hydrofluoric acid)

(continued)

Glasses made using silica (SiO_2) are noncrystalline ceramic materials. They share the same raw materials, structural characteristics and even physical properties as crystalline ceramics. For example, the fact that the chemical bonds are strong and directional means that they are poor conductors of heat and electricity and have a low dilatation coefficient. As there are no grain growth limits, they are more chemically stable and more resistant to corrosion.

In terms of mechanical performance, glass behaves in a unique way. A piece of window glass, for example, is brittle at room temperature but quite plastic when heated up for artisans to work with or heated up by automated machines. With the same behaviour as rubber, as amorphous material, it can be shaped by hitting it with a hammer (because it is able to absorb mechanical energy), but it becomes brittle after being immersed in liquid nitrogen (77 K).

8.2.1.1 Zachariasen Rules or Crystallochemical Theory

Structural models can be used to understand glass formation. Amongst them, Zachariasen rules, or *random network theory*, were the first to have a significant impact in glass science. Based on the outstanding glass-forming ability of silica, Zachariasen postulated that the ultimate condition for glass formation is the ability to form extended three-dimensional (3D) networks lacking periodicity, with energy content comparable (only slightly higher) with that of the corresponding crystal network. Its basic postulates are the similarity of interatomic forces, interatomic bonds and types of first coordination polyhedra between the glass and the corresponding crystal. Based on these postulates, Zachariasen stated four rules that make it possible to predict glass-forming ability:

1. Each oxygen atom in a glass is bonded only to one or two glass-forming cations (e.g. Si^{4+}, Ge^{4+}, B^{3+}, P^{5+}).
2. The coordination number of the glass-forming cation is small (and small means 3 or 4).
3. The oxygen polyhedra share corners, but not edges or faces.
4. Polyhedron structural units form a 3D aperiodic network in which every polyhedron shares at least three corners with its neighbours.

In crystalline and amorphous silica, short-range order is represented by the $[SiO_4]^{4-}$ tetrahedron, as a base with triangular edges, with an oxygen on each side and a silicon atom in the centre (Fig. 8.8). This basic building block has a cationic coordination number of 4 (rule 2), all the O–Si–O angles have the tetrahedral value of $109°28'$ and all Si–O bonds have the same length, ~0.162 nm. In silica glasses, all $[SiO_4]^{4-}$ are linked to all four corners, Q_4 (rules 3 and 4), to form a continuous 3D network, where each oxygen is shared between two silicons (which are bridging oxygens, BO) (rule 1). The Si–O–Si bridging angles exhibited a

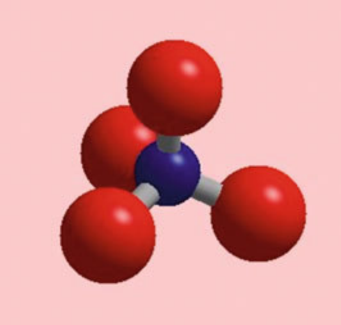


Fig. 8.8 Silica tetrahedron, $(SiO_4)^{4-}$, the basic building block of quartz and amorphous silica (*blue sphere* represents the Si atom and the *red spheres* the O atoms)

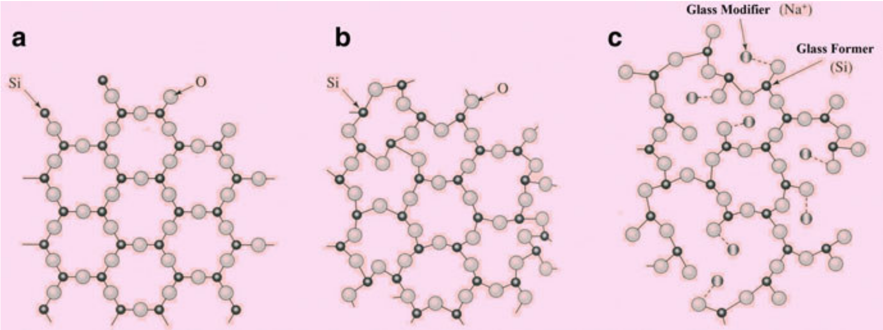


Fig. 8.9 2D diagram showing (**a**) quartz, (**b**) silica glass and (**c**) modified sodium silicate glass. The fourth oxygen atom of each tetrahedron, $(SiO_4)^{4-}$, is located either in front or behind the silicon atom, in relation to the diagram on paper

relatively broad (but not random) distribution, from 120° to 180°, which is an intermediate-range order feature of v-SiO_2, rather than a short-range order. Lack of long-range order is achieved by allowing a broad bridging angle distribution of siloxane (Si–O–Si) bonds, believed to range from ~120° to 180°. Rotation of adjacent tetrahedrons around each bridging oxygen and rotation of the tetrahedra around the line connecting bridging oxygens to a silicon atom also contribute to disorder (Fig. 8.9).

Zachariasen's rules exclude non-oxide glasses (e.g. in fluoride, chalcogenide and metallic glasses), chain-like oxide glass structures (e.g. metaphosphate glasses) and high coordination number oxide glasses. Zachariasen's rules predicted the existence of the main oxide glass formers (B_2O_3, SiO_2, GeO_2, P_2O_5, As_2O_5, P_2O_3, As_2O_3, Sb_2O_3, V_2O_5, Sb_2O_5, Nb_2O_5 and Ta_2O_5), although at his time, only B_2O_3, SiO_2, GeO_2, P_2O_5, As_2O_5 and As_2O_3 were made into glass.

Zachariasen also predicted the existence of glass modifiers (Na_2O, CaO, etc.). Although it is possible to produce glass using 100 % quartz (silica glass, SiO_2-v), the more common glass compositions contain alkali metal oxides (Na_2O, K_2O,

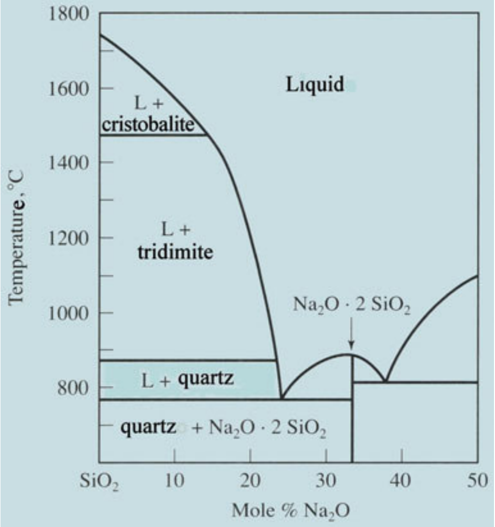


Fig. 8.10 Binary phase diagram of SiO_2–Na_2O

Li_2O, etc.) and/or alkaline-earth metals (CaO, BaO, etc.). These oxides have the important role of lowering the melting temperature of the mixture (and are known as *fluxes* in factory production), and in doing so, they reduce hugely the production costs (Fig. 8.10).

The structure of modified-silica glass can be viewed as a network of silica tetrahedra with occasional breaks in connectivity (Fig. 8.9c). Glass modifiers reduce the glass melting temperatures and melt viscosity by decreasing the connectivity and dimensionality of the glass former network. The breakage of siloxane (Si–O–Si) bonds originates non-bridging oxygen (NBO) species, where $Si–O^-$ provides charge compensation for the modifying cations. Alkaline ions are mobile and allow ion diffusion, whilst alkaline-earth ions are relatively immobile and hinder the diffusion of other ions, in particularly alkali ions, enhancing the chemical (and also the mechanical) resistance of the glass. These alkali ions occupy the interstices in the network, reducing the unoccupied free volume of the structure.

There is some evidence that the alkali ions are not randomly distributed throughout the network, but rather exhibit some degree of *clustering*, probably occurring in pairs near some non-bridging oxygens. The concentration of non-bridging oxygens increases with a decrease in the concentration of bridging oxygens, proportionally to the alkali (or alkali-earth) content, until a glass network can no longer be maintained and devitrification occurs.

Glass Formers

Elements: S, Se, P

Oxides: B_2O_3, SiO_2, GeO_2, P_2O_5, As_2O_5, Sb_2O_3, In_2O_3, SnO_2, PbO, SeO_2

Halides: BeF_2, AlF_3, $ZnCl_2$, Ag(Cl, Br, I), Pb(Cl_2, Br_2, I_2)

(continued)

Sulphurides: As_2S_3, Sb_2S_3, CS_2
Selenides: various components of Se, Sn, Pb, As, Sb
Tellurides: TeO_2, PbO e As_2O_5
Nitrates: KNO_3, $Ca(NO_3)_2$
Sulphates: $KHSO_4$
Carbonates: K_2CO_3, $MgCO_3$
Metals: Au_4Si, Pd_4Si (Fe–Si–B)
Polymers: polystyrene, polymethyl methacrylate, polycarbonate, polyethylene, nylon®

Silica is an excellent glass former, and silica glass formed more easily than silica crystal. Like silica, other good glass former compositions have high viscosity melts, where the atomic rearrangements occur slowly.

Note: A common nomenclature system known as Q_n notation expresses the concentration of bridging oxygens per tetrahedron by varying the value of the subscript n. A tetrahedron fully linked into the network via four bridging oxygens is designated as a Q_4 unit (like v-SiO_2), whilst an isolated tetrahedron with non-bridging oxygens is designated as a Q_0 unit. The value of n is thus equal to the number of bridging oxygens on a given tetrahedron. Determination of the five possible Q_n units (Q_0, Q_1, Q_2, Q_3 and Q_4 in silica-based glasses) therefore characterises the connectivity of the structure.

8.2.2 Raw Materials

Silicon is the predominant element in the Earth's crust (~75 % in total); it combines with oxygen to form silica (SiO_2) and with oxygen and other metals (alkalis and/or alkaline-earth metals) to form silicates. Most rocks contain silicates. Thus, as glass is a transparent structural material, the use of raw materials that contain contaminants that may opacify the glass is not appropriate. Only silica, with its high level of purity—as grains of rock or sand—enables the production of transparent glass.

Crystalline silica is a polymorphic substance, able to exist in different crystalline forms with the same chemical composition. Quartz, tridymite and cristobalite are some examples. In crystalline silica, the structural units ($(SiO_4)^{4-}$ tetrahedron, (Fig. 8.8) interconnect by joining vertices (Si–O–Si), where the 3D organisational diversity of these tetrahedron units leads to the different allotropic forms of silica.

Silica is a brittle, hard crystalline material; the chemical bonds that bind the tetrahedrons together are so strong that a temperature of over 1,723 °C (T_M) is needed to break them down. At these temperatures, the tetrahedrons constantly break down and are renewed, separating the tetrahedrons and allowing them to move around—the silica melts. This process of breakdown and renewal of the chemical bonds continues making the molten substance very viscous ($\mu = 1{,}013$ Pa). If the molten silica is slowly cooled, the tetrahedrons are rearranged three-dimensionally, re-establishing covalent bonds, and crystal is made. When silica cools quickly, the tetrahedrons are randomly immobilised and glass is made. This is why the density of an amorphous or vitreous structure ($d_{\text{vitreous silica}, 20\ °\text{C}} = 2.20$ g/cm^3) is always lower than the corresponding crystalline structure ($d_{\text{quartz}, 20\ °\text{C}} = 2.65$ g/cm^3; $d_{\text{tridymite}, 20\ °\text{C}} = 2.27$ g/cm^3; and $d_{\text{cristobalite}, 20\ °\text{C}} = 2.33$ g/cm^3). In vitreous silica, although the silica tetrahedrons share all their vertices with other tetrahedrons, they do not do this in a regular manner, so the structure does not have long-range order (Fig. 8.9b) (although it retains short-range order $(SiO_4)^{4-}$).

Although it is possible to produce glass with 100 % quartz (vitreous silica, SiO_2-*v*), the high melting point makes it so expensive that its use is limited to very specific technical applications, such as glass for use in laboratories and for optics and optoelectronics.

By adding fluxes to the molten glass (Na^+, Ca^{2+}, etc., which cannot form covalent bonds), it becomes less viscous and lowers the melting point, as well as reducing the T_g and the working temperature of the base-glass (Fig. 8.10). For example, whilst the T_M of pure silica is 1,723 °C, simply adding 33 % (mol) of Na_2O or 20 % (mol) of K_2O or even 66 % (mol) of PbO reduces the T_M to 789 °C, 769 °C or 714 °C, respectively.

Some Common Glass Compositions (% mol)

Fused silica	99.5 SiO_2
Window glass	73SiO_2 17Na_2O 5CaO 4MgO 1Al_2O_3
Aluminium silicate	62SiO_2 17Al_2O_3 8CaO 7MgO 5B_2O_3 1Na_2O
Fibreglass	55SiO_2 16CaO 15Al_2O_3 10B_2O_3 4MgO
Borosilicate (Pyrex 7740)	81SiO_2 13B_2O_3 10ZnO 4Na_2O 2Al_2O_3

The most common glass compositions contain oxides from alkali metals (e.g. Na_2O, K_2O, Li_2O) and/or alkaline-earth metals (CaO, BaO). These oxides are added through soda (Na_2O), potassium (K_2O) and lime (CaO). Soda is the most efficient flux, but if too much is added, it can compromise the chemical inertia of the glass. Potassium speeds up the process of glass corrosion through leaching in acid medium (see *Glass Corrosion*). The fluxes are added in carbonate form; as they break down, they form oxides and release CO_2. The lime is added as limestone or dolomite (which also contains magnesium carbonate) and the soda as sodium carbonate. Currently, sodium carbonate is produced using the Solvay method, but previously it was added in the form of plant or animal ash.

Today a raw material that should not be overlooked is *cullet* (pieces of waste glass). *Cullet* is used on an *industrial* level when it is a waste by-product of the manufacturing process and on a *domestic* level when it is taken from waste left from pieces used for domestic or restoration purposes. In the manufacture of *float* (see *Float*), glass up to ~ 20 % (wt) of industrial *cullet* can be used; in the production of container glass, the use of *cullet* is not restricted to just industrial *cullet*, and up to 90 % wt can be used. In addition to *cullet* (or instead of it), some *float* glass production uses blast furnace slag (metallurgy) as a raw material.

The granular distribution of each raw material is dependent on its molten viscosity. For example, quartz should have larger grain size than all other raw materials, as it should be the last raw material to be melted and then the last to be incorporated into the molten bath. As SiO_2 is an excellent glass former, its melt is very viscous. By retarding the SiO_2 incorporation into the molten bath, it will keep the viscosity of the molten material low for longer, thus helping the *homogenisation* and *refining* processes (see *Glass Flow Chart*). The *cullet* is added with coarser grains than all other raw materials.

Now it is clear why window glass, container glass and glass for vehicles have a modified-silica-based composition, whilst glass crucibles are made of pure silica glass (100 % SiO_2). The high operating temperature of the crucibles (e.g. $T \sim 1{,}700$ °C) means there are no modifiers, so a glass with a high T_g is produced. For other purposes, the relatively low working temperature allows modified silicate glass is to be used, with low T_g levels as well as low processing temperatures, which reduce the cost of production.

In spite of its excellent physical properties, the use of silica glass is limited due to its high cost. As a result of applications that required high operating temperatures, for example, on doors or plates of domestic ovens, it is common to use glass ceramics. For fire-resistant purposes, *laminated glass* is used.

Pyrex® glass (a registered *Corning* brand), which is made using two components, SiO_2 and B_2O_3, and two modifiers, Na_2O and CaO, has physical properties between those of silica and silica-based glasses. With Pyrex® glass, the low coefficient of thermal expansion creates a glass with three times as much resistance to heat shock than modified silica. Pyrex® glass is used for test tubes and household glass objects (for use over hobs and in the oven), as it can tolerate temperatures ranging from melting ice or flames.

Nowadays, besides traditional silica-based glass, it is possible to produce glass using practically any material. Metallic glasses can be produced using metal bonds or vitreous polymers, covalently bound where secondary chemical bonds play a key role.

Metals used to produce glass are metal alloys, typically 80 % (mol) of one metal and 20 % (mol) of a semimetal, with a relatively low melting point. $Cu_{80}Zr_{20}$, $Au_{80}Si_{20}$, $Fe_{78}Si_9B_{13}$ and $Fe_{32}Ni_{36}Cr_{14}P_{12}B_6$ (Metglas®, an *Allied Chemical* registered brand) are some examples.

Metals are perhaps the hardest materials to vitrify. As they are not very viscous in their molten state, they enable high atomic mobility; with fewer elements in the chemical composition and with simple crystalline networks (preferably *cfc*, *ccc*, *hc*), the crystallisation process is easier. A very high cooling speed is needed to obtain vitreous metals around 10^8 °C/s.

The operating temperature limit for metallic glasses is low, around just a few hundred degrees, so the atoms crystallise as they acquire some mobility. As there are no grain growth limits, metallic glasses are more resistant to corrosion.

Metallic Glass with a Semimetal

- The introduction of a semimetal in the alloy composition reduces its T_M, lowering the temperature interval that the material needs for rapid cooling from T_M to room temperature.
- The size of the single unit increases so the atoms have to travel further to find their equilibrium positions in the network, taking longer to crystallise.
- The crystal energy increases as the crystalline network distorts to accommodate the differently sized semimetal.

8.3 Glass Technology

8.3.1 Melting, Homogenisation and Fining

The furnace batch is formulated according to the chemical composition of the glass to be produced (Table 8.1). The raw materials are weighed, mixed and preheated. After introducing them in the furnace, they are heated until a liquid, viscous paste is obtained. In glass process, a batch methodology was common. Today the glass production process is continuous, the raw materials are added continuously to the furnace entrance, and the glass is extracted just from the opposite side of the furnace.

Of all the raw materials, *cullet* is what remelts at the lowest temperature, which speeds up the melting process. Remelting *cullet* saves energy as sand, sodium and lime do not need to be melted down. That is why the amount of energy needed in the glass process decreases with the amount of *cullet* added. The energy needed to melt (q) in kJ/kg of glass can be estimated using the following equation (where the parameters of the equation are based on the melting of a soda-lime glass composition):

$$q = \pm 4800 - (1200 * b)/100 \tag{8.1}$$

where b is the percentage of *cullet* in the furnace. From Eq. (8.1), fuel reduced by ~2.5 % for every 10 % of cullet added. In practice, the melting is speeded up by adding more *cullet*.

Fluxes, besides reducing the typical temperatures of glass (T_M, T_g and ΔT for work), also reduce the surface tension of the melted glass (σ) (helping gas bubbles formation, as shown in Eq. (8.2)), increase heat conduction in the molten glass and enable melting to take place at lower temperatures.

The pressure p required for a spherical gas bubble to form with a radius of r, in a liquid with surface tension σ, is calculated using the equation:

Table 8.1 Typical glass batch

Batch composition			Molten glass composition (wt%)					
			66.51 Sand (99.2% SiO_2)	9.04 Feldspar (65.6% SiO_2, 17.8 % Al_2O_3 10.3 % Na_2O, 6.3% K_2O)	19.82 Sodium carbonate (Na_2CO_3)	1.86 Potassium carbonate (K_2CO_3)	10.82 Dolomite (21.9 % MgO 30.3% CaO)	11.55 Lime ($CaCO_3$)
Oxide	% Mol	% wt	% oxides incorporated by raw material					
SiO_2	71.81	71.91	65.98	5.93				
Al_2O_3	0.95	1.61		1.61				
Na_2O	12.12	12.52		0.93	11.59			
K_2O	1.17	1.84		0.57		1.27		
MgO	3.52	2.37					2.37	
CaO	10.43	9.75					3.28	6.47
			Weight of each raw material (as reference 100 proportions of sand)					
	100.00	100.00	100.00	13.59	29.80	2.80	16.27	17.37

$$p = \frac{2\sigma}{r} \tag{8.2}$$

whereby it is difficult to form bubbles with a small radius.

During the melting process, different chemical reactions take place, one of which is breaking down/dissolving (as carbonates and sulphates), as well as dehydration (of hydrate salts) and other solid states, involving reactions/changes between other components. The breaking down of carbonates produces small bubbles of carbon dioxide (CO_2), as the glass melts. As the molten vitreous material is quite viscous, these bubbles are hard to remove (as they rise to the surface of the bath where they escape into the atmosphere). In small-scale production furnaces (100–200 kg), it is not hard to remove these bubbles; however, in modern factory equipment (with 200–600 tonne furnaces), it can become a problem. To speed up the process of releasing gas bubbles, CO_2 (refinement) sodium sulphate is added. The sodium sulphate rapidly releases sulphur dioxide as shown in Eq. (8.3) (for $T > 900\ ^\circ C$):

$$2Na_2SO_{4(s)} \Leftrightarrow 2Na_2O_{(s)} + 2SO_{2(g)} + O_{2(g)} \tag{8.3}$$

Although at first glance adding more gas bubbles to the molten vitreous material may not appear to make sense, the fact is that the bubbles formed (with sulphur dioxide composition) are larger in volume (and chemically different from the smaller gas bubles present in the molten bath), thus absorbing the carbon dioxide dissolved in the molten bath. The bigger bubbles rise more quickly, speeding up the refinement process as shown in (8.4). The hydrostatic rising of gas bubbles in the molten material is quantified using the Stokes equation:

$$v = \frac{2}{9} r^2 g \frac{\rho_1 - \rho}{\eta} \tag{8.4}$$

where v is the ascending speed of the gas bubble, r is its radius, g the increased gravitational speed, $\rho_1 - \rho$ is the difference in density between the glass and the gas in the bubble and η is the viscosity of the glass.

The maximum temperature reached in the furnace is around 1,600 °C (*hot spot*). After the homogenisation and fining processes (where the glass is chemically homogenised and bubbles are removed), the molten batch rested for a while and then undergoes thermal conditioning (where it is thermally homogenised). After decreasing its temperature to around 1,100 °C, the glass can be moulded.

The glass melting process consumes a lot of energy. The energy consumption for continuous glass production is normally 5–10 MJ/kg of glass, which means that in order to produce 1 kg of glass, 5–10 MJ of natural gas, fuel or electricity are needed. Over the last few decades, there has been a drop in energy costs for glass production, which is mostly due to improved heat insulation in the furnaces and more efficient combustion, the preheating of raw materials and the use of *cullet*. As well as providing energy, this has environmental benefits, such as reducing the use of natural resources, municipal solid waste (MSW), gas emissions, etc. Using 100 kg of *cullet* can save 120 kg of primary raw materials. This 20 % difference corresponds to a loss of gas as carbonates or sulphates are broken down as it melts.

8.3.2 Flat Glass-Forming Techniques

8.3.2.1 Roman Glass

The molten glass is poured out onto a flat slab, where it is stretched into the desired shape. The glass panels produced are relatively thick but allow light through without distorting the image. This technique, which was developed by the Romans, was used to produce flat glass until the Industrial Revolution (nineteenth century).

8.3.2.2 Mediaeval Glass

A hollow piece of glass is cut with tongs and then immediately blown using a blow tube and flattened out over a table. Various pieces of glass are then cut into smaller pieces which are mounted in a metal tin structure, creating a stained glass window. Colouring the glass is done on *bulk* (during the melting process) or by manually painting onto the glass surface. This technique, which developed during mediaeval times in Europe, was used until the Industrial Revolution (nineteenth century).

8.3.2.3 Crown Glass

Today the English term *crown* is used generically for soda-lime glass. The term *crown* comes from a manual method used for producing flat glass—a piece of glass is supported in a blow tube and quickly rotated to create glass pieces in disc or *crown*-shaped pieces.

Manual methods for producing flat glass are still used today, for example, when glass is required for restoration purposes.

8.3.2.4 Colburn-Libbey-Owens Glass

Continuous flat glass production was patented in 1902 by Colburn. The method consists of vertically stretching a sheet of glass using a shallow tank of molten glass. Two sprockets, cooled with water, secured the edges of the glass sheet and stretched it vertically. After stretching it 60–70 cm, during which time it cooled down, it was folded over and laid out horizontally over a flattening table. After being flattened, the sheet of glass was polished on both sides (Fig. 8.11).

8.3.2.5 Fourcault-Pittsburgh Glass

During the same period, Fourcault developed a vertical draw method for continuous glass production. The main differences compared to the Colburn process are: (1) the part used to stretch the glass piece, as Fourcault's process uses a die immersed in the molten vitreous material, and (2) the fact that the whole process takes place vertically, including the annealing and cutting of the glass sheet. After annealing, the glass sheet is polished from both sides (Fig. 8.11).

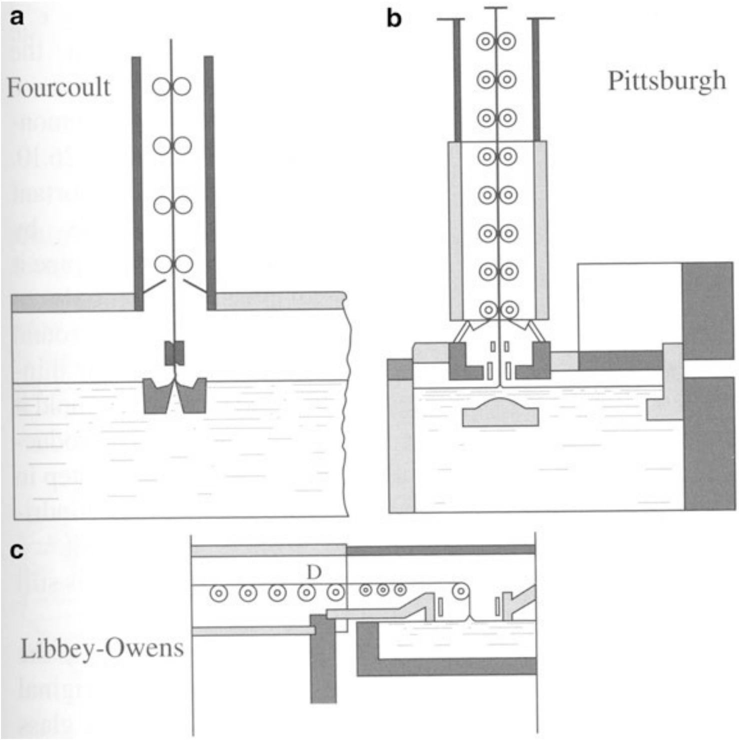


Fig. 8.11 Continuous flat glass production: (**a**) Fourcault, (**b**) Pittsburgh and (**c**) Libbey-Owens

8.3.2.6 *Float* Glass

In 1952, Alastair Pilkington, the technical director of the family business Pilkington Brothers (UK), developed a *float* glass process, a technique which would revolutionise the flat glass process from the 1960s onwards. The *float* technique represented the biggest advance since the invention of *blown glass* in 200 BC. Alastair Pilkington was knighted in 1970 in recognition of the benefits he had brought to technology and the British economy.

Until then, flat glass had been produced using a process where sheets of glass were mechanically stretched; the sheets of glass produced were left with marks where the rollers had been in contact with them (the Colburn-Libbey-Owens system) or were distorted (using the vertical stretching methods introduced by Fourcault or Pittsburgh). Production costs were high, mostly due to the final polishing of the sheets of glass. The *float* method produced flat glass with an excellent surface finish on both sides (avoiding any latter polishing process), reducing both the time and costs required to produce it.

Besides the more traditional applications of glass in the building and vehicle industries, *float* glass is used in the aeronautical industry, for windows for commercial planes to the most sophisticated military jets, heat shields on guided missiles, submarine periscopes and in the Challenger project.

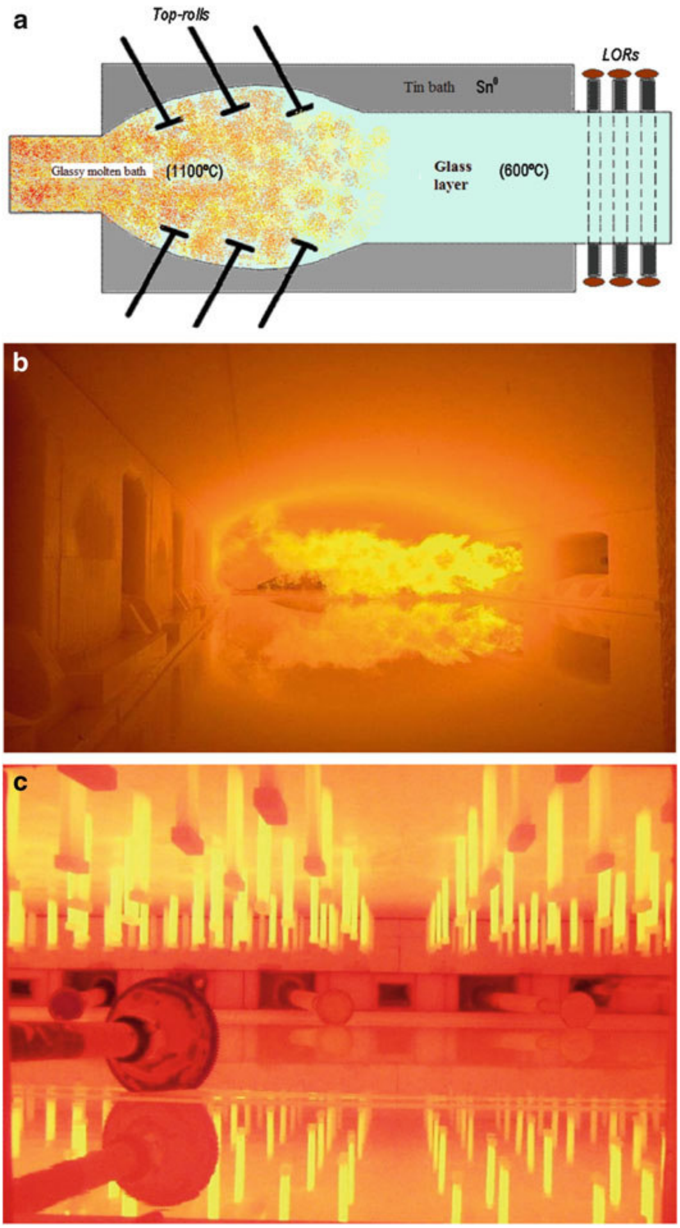


Fig. 8.12 *Float* unit: (**a**) outline of the *float* chamber; (**b**) photography of the *float* chamber; (**c**) photography of the top roller

Float glass is formed by pouring the molten glass (~1,150 °C) over a metallic tin bath (Sn^0), about 30 cm deep (Fig. 8.12), forming a (*floating*) thin glassy layer. In order to avoid tin oxidation (formation of S^{2+} and S^{4+} species), the *floating chamber* is kept under a strong reductive atmosphere (nitrogen (N_2) with 0.5 % hydrogen (H_2)). Both the glass, which is very viscous at this temperature ($\eta \sim 10^3$ Pa s), and the molten tin, which is quite fluid, are immiscible and have a flat interface. A sheet of glass forms over the top of the molten metallic tin and spreads over it *floating* and then cools and solidifies. After leaving the *float* unit, the glass is immediately annealed and cut.

The important and original element of the *float* process in the manufacturing of flat glass is the chance to obtain flat pieces of glass that are polished on both sides without the need to polish them afterwards. On the surface that is exposed to the air, the sheet of glass is heat polished, and on the surface in contact with the molten tin, it ends up with a specular polish.

8.3.3 Annealing

The glass takes shape during the rapid cooling process, turning from a viscous and easily malleable state to a vitreous state over a short period of time (Fig. 8.13). As the temperature drops and the viscosity increases, the ionic movements become slower, preventing the diffusion needed to form crystal. The glass then retains a state with high inner tension, which makes it susceptible to brittle fracture, for example.

From an industrial perspective, the melting point is defined as the temperature at which the viscosity has a value of 10 Pa s. The work area, where the vitreous substance can be shaped, is limited by the viscosity values 10^3 and $10^{6.5}$ Pa s.

During the rapid cooling process, due to the poor heat conduction in glass, the release of heat does not occur at the same rate throughout the glass sheet, establishing a temperature gradient from the centre (of the glass pane) to the surface. The outer layers, which cool faster, become rigid and contract, whilst the internal layers remain hotter and more viscous. As the temperature gradient drops (through a homogenising heat treatment), the inner layers contract, but they do not

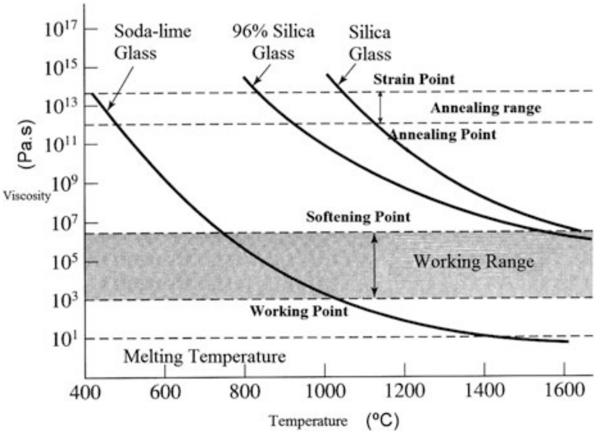
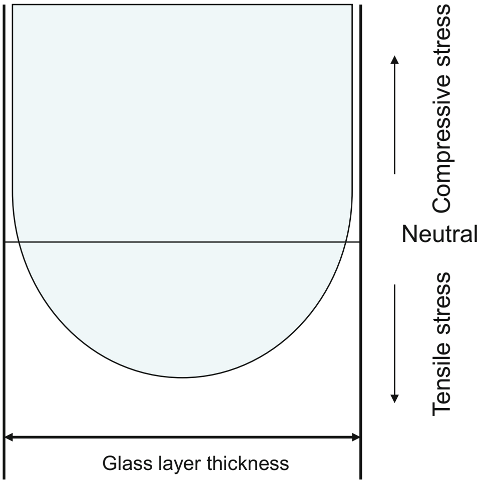


Fig. 8.13 Viscosity–temperature graphs for silica and sodium–calcium glasses

Fig. 8.14 Stress gradient from the centre of the glass sheet to the surface



do this freely as there is opposition from the rigid surface layers (that push them outwards, preventing them from reaching the required dimensional stability driven by the expansion coefficient). In thermal equilibrium, the inner layers remain under tensile stress and the outer layers under compressive stress (Fig. 8.14).

In industrial practice, after forming, the glass is cooled slowly to reduce internal tension. This cooling process is known as *annealing*.

Annealing is the single operation used to lower the internal free energy of the glass. After annealing, the structure is relaxed in the most uniformly way possible and acquires the same specific volume at all points.

8.3.4 Flow Chart of *Float* Glass Production Process

RAW MATERIALS

MAIN:

Sedimentary rocks, sands, sandstones, quartz and quartzites, dolomite, lime, felspar, sodium sulfate, carbon and cullet.

Raw materials, with suitable particle size distribution, are weighed and mixed with the cullet. The mixture is then introduced into the furnace.

↓

MELTING AND FINING FURNACE

Raw materials will mix with the molten batch and melt, at a temperature ~ 1550 ºC. During the initial stay at the furnace the temperature is around ~1100 ºC, and homogenization and finning take place.

MELTING T ~ 1550 ºC $\eta = 10$ Pa.s

FINNING T ~ 1100 ºC $\eta = 10^2$ Pa.s

WAY OUT T ~ 1050 ºC $\eta = 10^3$ Pa.s

↓

FLOAT

The molten glass leaves the melting furnace and enters the *float* chamber, where it *floats* over tin bath (Sn^0). From the *float chamber* entrance to the exit the temperature will decrease from 1050 ºC to 600ºC.

The glass sheet thickness (between 3 and 25 mm, *standard*) and the glass sheet width (maximum 3210 mm) are controlled by the lateral *top rollers* speed pull.

(continued)

FLOAT

T $_{START}$ ~1050 °C η = 10^3 Pa.s

T $_{END}$ ~ 650 °C η = 10^9 Pa.s

REDUTIVE ATMOSPHERE N_2

TIN BATH Sn^0

↓

COATING*

Coatings grant glass particular optical or termal performance (ex., *ANTI-REFLECTION GLASS*, *MIRROR GLASS*, *LOW E* GLASS). Chemical vapor deposition (CVD) occurs *on-line* inside the *float chamber*.

↓

PATTERNING*

ROLLED PLATE GLASS is produced by stretching and rolling the glass after it is produced (*offline*). When it is rolled a motif is pressed on using one of the rollers.

↓

ANNEALING

In the *annealing chamber,* the glass is slowly cooled down from 600 ºC to ambient temperature, in order to minimize internal stresses.

After annealing, the glass sheet can be cutted and stored.

↓

CUTTING AND STORAGE

(continued)

After annealing, the glass is optically checked by laser, classified and ordered, accordlingly to the level of quality.

Then the glass sheets are automatically cutted (6 m × 3,21 m, *standard*) and stored in the factory warehouse.

* - MARKED OPERATIONS ARE NOT MANDATORY, BEING PRESENT ONLY FOR PARTICULAR GLASS TYPES

NOTE: COLOR IS AN OPTION. IN FLAT GLASS DYES ARE INTRODUCED INSIDE FURNACE.

COLOR:
GREEN: IRON, CHROMIUM OXIDE
BLUE: COBALT AND COPPER OXIDE
VIOLET: MAGNESIUM OXIDE
AMBAR: IRON AND SULFUR
RED: SELENIUM AND CADMIUM SULFATE

8.4 Glass Properties

Unlike cement, wood and heterogeneous composite materials, glass is homogeneous even on a molecular scale. Although metals are macroscopically homogeneous, they are formed of microcrystals.

Glass is isotropic so its properties do not depend on directionality. Cement and metals are also isotropics, unlike composite materials, whose properties depend on the direction in which the fibres are positioned.

8.4.1 Optical Properties

Glass is traditionally the transparent material used in architecture. The choice of glass for architectural projects is, in most cases, made for its optical performance.

Light interaction with transparent materials occurs through different processes as illustrated in Fig. 8.15. The *incident ray* can be *reflected* (R) off any surface. The light that passes through it can be *scattered* (S) or *absorbed* (A). Part of the light absorbed can be reemitted in a phenomenon known as *fluorescence* (F). And, finally, the light that passes through the material is *transmitted* (T).

Excluding fluorescence, light interaction with a transparent material can be classified in the following way:

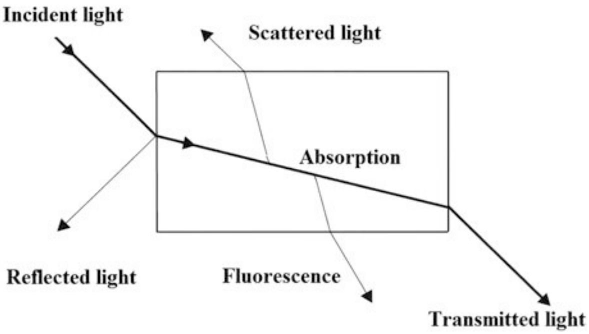


Fig. 8.15 Light interaction with transparent materials

$$1 = R + S + A + T \tag{8.5}$$

In materials with good optical quality, the light fractions scattered (S) and absorbed (A) can be disregarded:

$$1 = R + T \tag{8.6}$$

8.4.1.1 Reflection

Specular Reflection

When light hits a smooth surface, the light is reflected specularly (an incidental fraction of light is reflected off the surface at an angle that is equal to the angle of incidence, so that the incidental ray, the reflected ray and the normal ray reflected from the surface at the point of incidence along the same plane). This is the phenomenon found in mirrors and polished surfaces. It is the regularity of specular reflection that allows images to be displayed in mirrors.

The fraction of light that is specularly reflected off a surface depends on the refractive index of the material according to the Fresnel formula (valid for normal incidence with transparent materials):

$$R \approx \left(\frac{n_2 - n_1}{n_2 + n_1}\right)^2 \tag{8.7}$$

where R—specular reflection, n_1—refractive index of medium 1, n_2—refractive index of medium 2.

When the light is transmitted, for example, through a vacuum or from the air to inside glass in a window, then

$$R \approx \left(\frac{n_s - 1}{n_s + 1}\right)^2 \tag{8.8}$$

the refractive index of the air is approximately 1.

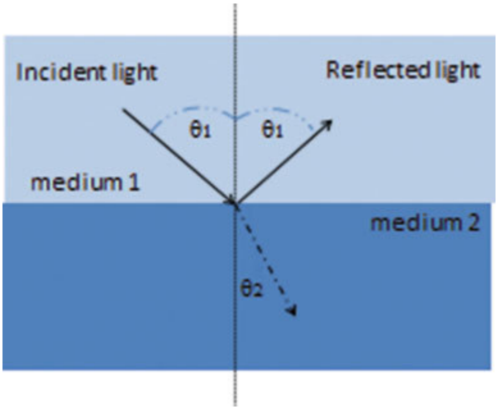


Fig. 8.16 Specular reflection

The bigger the refractive index of a solid, the bigger the specular refraction. For example, the high refractive index of diamond ($n_D = 2.43$) means that when it is multifaceted, it shines brightly due to multiple reflections ($R = 17.4$ %). The same is true of lead crystal ($R = 18.4$ %), which has a refractive index ($n_D \sim 2.50$) significantly higher than normal window glass ($n_D \sim 1.5$) with a surface reflection of 4 %; so whenever a ray of light passes through a glass–air surface, its intensity is reduced by 4 % (Fig. 8.16). With window glass, after the reflection on the first surface, the luminous intensity is reduced to 96 %. After passing though the second surface, it is reduced by 4 % again (now 0.04 of 96 %), so the fraction of light transmitted will only be 92.16 % of the incident ray.

If instead of glass a gap with *double glazing*, there are four reflective surfaces, so the radiation transmitted will only be 84.90 % of the incident ray.

Some architectural and civil engineering projects try to minimise the reflective component; for example, in commercial displays or museum exhibits, anti-reflection glass is used. To reduce the loss in reflection, it is common to coat the glass with a material whose refractive index is lower than the glass underneath and with a thickness around 1/4 thickness of radiation waves in order to allow destructive interference between the glass reflection and the film reflection (Fig. 8.17).

In other architectural solutions, the opposite is intended, i.e. to minimise the transmission component at the cost of the reflection component. This is often the solution used for outer surfaces of service buildings, with *mirror glass*. The effect of *mirror glass* is created by a special surface coating on the glass with a refractive index higher than the glass underneath.

Another type of glass in architecture is high solar control glass. This category includes glass with a silver, nickel or gold film coating on the surface that is very efficient for reflecting infrared (IV) and ultraviolet (UV) rays.

Diffuse Reflection

When a beam of light hits a bumpy surface, the reflected component is diffused more the rougher the surface is (Fig. 8.18). The diffuse reflection increases as the

Fig. 8.17 Anti-reflection glass. Light reflected by the glass surface is 180° or $\lambda/2$ antiphase relatively to the light reflected by the glass coating, as it passes over twice the coating thickness $\lambda/4$

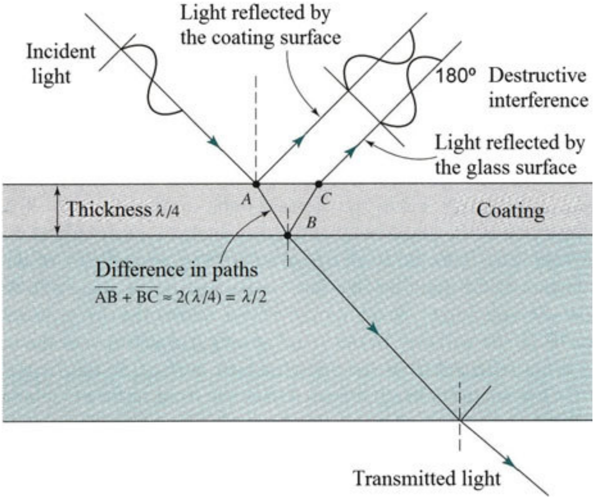
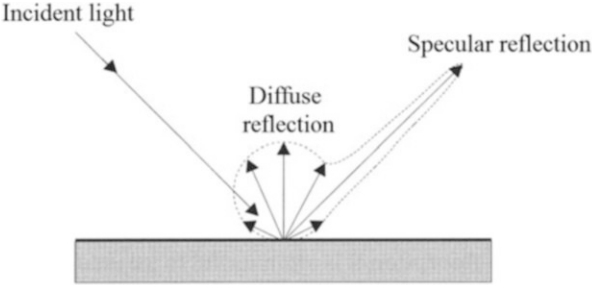


Fig. 8.18 Diffuse reflection in bumpy surface. The diffuse reflection increases as the specular reflection decreases



specular reflection decreases. A surface made out of fine grains only provides the diffuse reflection component unlike a mirror surface which only has the specular reflection component.

$$R = R_{\mathrm{DIFUSE}} + R_{\mathrm{SPECULAR}} \tag{8.9}$$

Mixed Reflection

Mixed reflection combines specular and diffuse reflection, which is more realistic. This is why the diffuse reflection component associated with the specular reflection component determines the appearance of a solid. The shininess of a surface is caused by this.

Architectural projects can use glass with a high diffuse reflection component, as is the case with *open spaces*, where it is common to use *rolled plate glass* or *silkscreen printed glass*.

8.4.1.2 Refraction

When light passes through transparent interfaces (between mediums with different densities), for example, air/water or air/glass, not only is the direction of the beam of light changed but also its phase velocity and wavelength change abruptly between them. This phenomenon, which is known as light refraction, is responsible for distorting the image of objects immersed in cups of water, inside swimming pools, aquariums or even objects near to the ground on really hot days (near to the ground, the refractive index will be higher, decreasing as we move away from it).

The easiest way to describe the refractive index is through the relationship between the speed of light in a vacuum and the speed of light in air:

$$n = \frac{v_{\text{vácuo}}}{v_{\text{mat}}} \tag{8.10}$$

If i represents the angle of incidence and r the angle of refraction, these are related to the speed of light in a vacuum, v_{vac}, based on the refractive index, n, according to Snell's law:

$$n = \frac{\nu_{\text{vac}}}{\nu_{\text{mat}}} = \frac{\lambda_{\text{vac}}}{\lambda_{\text{mat}}} = \frac{\sin i}{\sin r} \tag{8.11}$$

In glass, the index refraction is independent of direction, but is a function of radiation wavelength. In general, the refraction index decreases when the wavelength increases, and for the same material, the infrared refractive index is lower than the ultraviolet refractive index. This is the phenomenon that causes rainbows.

8.4.1.3 Scattering

Scattering occurs whenever small crystals or other heterogeneities are present in the glass. Current *float* glass production enables the production of flat glass free from these types of defects (mass defects). Generally, scattering is undesirable, but sometimes the phenomenon can be exploited. *Opal* and *ruby* glass are examples of this, deliberately manufactured with scatter centres. Scattering is maximised whenever the diameter of the particles is around the length of the radiation wavelength (around 400–700 nm for visible scattering).

8.4.1.4 Absorption

When light hits a glass and the glass transmits it at all frequencies, the glass is colourless. However, if the glass absorbs light differently depending on frequency, the glass appears coloured.

When scattering is absent and the centres of absorption are evenly spread across the material, we may calculate the light absorbed using the Lambert-Beer law:

$$I = I_0 \exp(-\alpha_{\text{a}} l) \tag{8.12}$$

where I is light intensity on transmission, I_0 incidental transmission, l optical thickness and α_{a} the linear absorption coefficient. The coefficient of absorption varies significantly with the frequency, within visible light range. Glass with excellent optical performance has α_a values as low as 0.002 cm^{-1}, with values of 0.04 cm^{-1} common.

The main components of glass are colourless, so colouring agents need to be added (usually by adding frits) to produce coloured glass. The use of metal oxides creates a purer colour, compared to coloured glass produced using paint or surface coatings.

For laminated glass, for example, the colour can be easily incorporated in the synthetic polyvinyl butyral (PVB) coating. However, the use of colour in the glass adds greater durability and a better aesthetic effect.

8.4.1.5 Translucence, Opacity

Transparency is an optical property that enables clear image transmission. A material that is not transparent but which still allows light through is translucent. In this case, the light transmitted has a specular component and a diffuse component (Fig. 8.15):

$$T = T_{\text{diffuse}} + T_{\text{specular}} \tag{8.13}$$

When there is a total loss of transmitted light, the material is defined as opaque.

Many types of glass and glazing contain opacifying components that form a second refractive index phase over the base glass ($n_D \cong 1.5$). The level of opaqueness caused by the existence of a second phase, such as pores or (micro- or nano) particles, depends on the average size and concentration, as well as the difference between the refractive indexes.

8.4.2 Mechanical Properties

8.4.2.1 Stress and Strain

All materials change shape and/or size when subjected to tensile forces. This phenomenon is called strain and results from a combination of many deformations occurring in the material's chemical bonds. The extent of deformation will depend on the arrangement of the atoms and the type of chemical forces present.

For low levels of tensile stress, stress and strain are related linearly exhibiting a proportionality constant—Young's modulus, E (i.e. resistance to deformation). In this regime, a material under tensile stress resumes its initial size and form when the tensile stress is removed. A material with a low-E value has a high level of deformation even for low tensile levels (e.g. metals). High E values are associated with very rigid materials (i.e. with high resistance to deformation such as glass and ceramics).

The tensile stress where deformation cannot be reverted is known as yield strength and corresponds to the elastic limit. This stress value is sometimes hard to identify, and so the test stress is used, which corresponds to the point where the strain is 0.2 % higher than the elastic limit (strain is 1.002 times higher than elastic

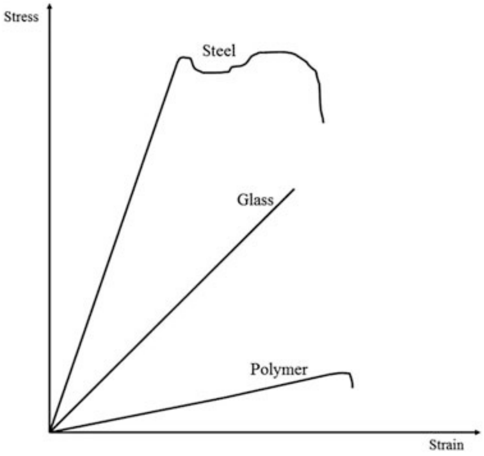


Fig. 8.19 Stress and strain curves for glass, metal and polymeric materials

deformation, calculated by linear extrapolation). For stress values over the yield point, some materials are permanently deformed—this is known as plastic deformation (Fig. 8.19). This is where chemical bonds are broken down and glasses and ceramic structures collapse. (Metals have mechanisms that allow the absorption of mechanical energy—the linear defects, *dislocations*.)

Glass does not deform plastically, but breaks as soon as it is out of its elastic domain (Fig. 8.19). The stress–strain curve of glass reflects its mechanical behaviour:

1. The linearity of elastic range allows that:
   - When stress is applied and removed, the piece of glass recovers its shape and initial size exactly.
2. The lack of plastic deformity leads to:
   - Brittle fracture. Materials with a large amount of plastic deformation before breaking are known as ductile; those that break without any plastic deformation are brittle. The lack of grain boundaries and dislocations (linear defects present in crystalline metals) causes a lack of resistance to crack propagation, so a crack can develop even at low levels of stress. Catastrophic fracture is therefore typical in glass.
   - Toughness. A material's impact strength is greater the more elastic energy is absorbed before breaking. This depends on the area within the stress–strain curve. In the absence of plastic deformation, the area within the stress–strain curve is small, so the glass is very susceptible to breaking under an impact.
   - Absence of fatigue. As structural rearrangement cannot take place on a structural level, glass cannot suffer fatigue (unlike metals).

- Susceptibility to too much tension applied to one area, due to the inability to absorb energy and plastically deform. Metals have a natural mechanism of energy absorption—moving in many slip rate systems. Glass cannot undergo structural rearrangements on an atomic level, so the glass has catastrophic (brittle, explosive) fractures. This issue is particularly important at glass fixture points. Any load to be applied should be distributed as evenly as possible (i.e. spread over the biggest area) and preferably over a material that is able to absorb the load and deform. The main objective of glazing materials is to avoid contact between the glass and other surrounding hard (and brittle) materials and be able to absorb the applied load.
- Fragility, due to an inability to absorb energy, and plastically undeforming make the glass more susceptible to cracks. A steel structure can take local stress and redistribute it in small plastic deformations. Glass cannot do this; it deforms elastically until the point where the chemical bonds break and create a crack.

8.4.2.2 Brittle Fracture

Rupture strength, calculated based on the strengths of the chemical bonds, is around 20,000 N/mm^2 for silica glass. In practice, the stress needed to break glass is much lower than in theory. A glass windowpane, for example, has a rupture strength around 100 N/mm^2, with the break usually occurring on the surface of the glass.

The microcracks on the glass surface can explain this phenomenon. The development of a crack creates two new surfaces, which demands a certain amount of energy; when elastic deformation energy accumulates around the crack, it exceeds the energy value needed to create two new surfaces, thus providing the conditions needed to propagate the crack. The energy of elastic deformation can be turned into surface energy, creating new surfaces. According to A. A. Griffith (1893–1963), for a break to happen, energy released in deformation should at least be equal to the energy spent in creating new surfaces:

$$\sigma = \sqrt{\frac{2E\gamma}{\pi a}} \tag{8.14}$$

which relates the fraction tension σ needed to create a crack with the modulus of elasticity, E; the surface energy of the crack, γ; and the behaviour, a, of the crack.

For cracks that are smaller than the critical figure, the energy from the formation of new surfaces exceeds the energy gained from releasing the stress, thus a crack does not spread and the glass does not break. On the other hand, if the cracks are equal in length or longer than the critical figure, the energy from the release in tension exceeds the energy cost of the increase in surface energy, so the crack grows significantly and gives rise of a catastrophic fracture.

Griffith's criterion only applies to brittle materials, unable to undergo plastic deformation, i.e. where the work on the material creates new surfaces.

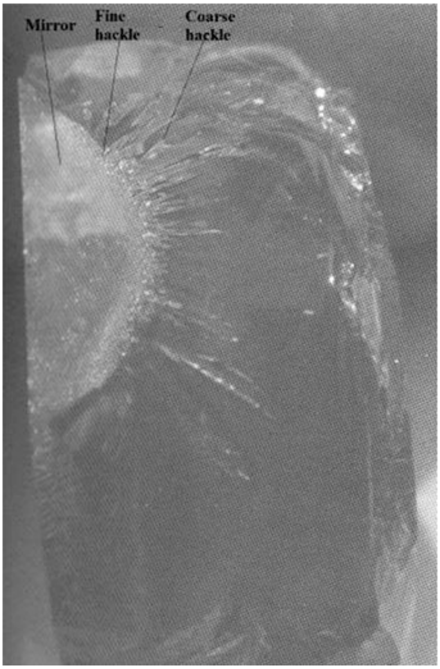


Fig. 8.20 Fracture pattern in *float* annealed glass

Fracture Pattern (Annealed Glass)

In glass, the crack normally starts from a microcrack on the surface and has a fixed origin point (Fig. 8.20). Originally elastic stress (of a higher intensity than a given critical value) and the presence of a crack (also longer than a critical value) combine to create a catastrophic fracture.

The crack starts relatively slowly but increases the more stress is applied. Around the source, the crack spreads relatively slowly. As the speed at which it spreads increases, the surface of the fracture becomes unstable (mixed area). The speed at which it spreads is higher and the crack is compounded (rough area). At each new ramification, the speed of the crack is reduced. If the stress is higher, a new ramification occurs. The number of ramifications gives us an idea (even if it is qualitative) of the energy or intensity of the stress that caused the crack. A simple crack suggests low energy stress; multiple ramifications suggest high stress or high energy.

Fracture Pattern (Tempered Glass)

As Griffith cracks are only created when subjected to a tensile force (over a given critical value), glass under compression exhibited higher mechanical strength. Any (external) applied tensile stress will have to exceed compression (internal and surface) before being used for the crack growth.

In *tempered glass*, there is an outer layer under compression (~20 % of the thickness of the glass on each surface) and an inner layer under tensile forces (corresponding to the remaining 60 % of the thickness). The stress under compression is additive; thus if a piece of glass were to fracture at a tensile force of 30 N/mm^2,

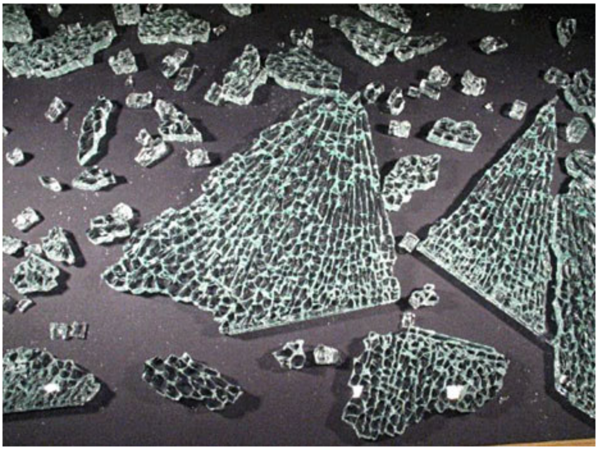


Fig. 8.21 Fracture pattern in *tempered glass*

once tempered (with an outer layer in compression of, e.g. 70 N/mm^2), the new fracture stress will be 100 N/mm^2.

In *tempered glass*, if a crack reaches the inner area under tensile force, the fracture becomes explosive. The high elastic stress available (since the gap beat the compressive strength) allows the fracture to propagate violently, which will lead to a very high number of ramifications, forming the fractures that are characteristic of *tempered glass* (Fig. 8.21). Another advantage of *tempered glass* is that the pieces do not have sharp edges.

Tensile stress (inside) of 45 N/mm^2 (related to a compressive stress of 90 N/mm^2) causes ramifications in the fracture every 6 mm and creates a large number of fragments.

When, in *tempered glass*, the fracture does not originate from the edge, it is called a *butterfly pattern fracture*. In this case, the fracture starts from opposite sides, creating two pieces, twice the size of the remaining pieces, which contain the source of the fracture.

8.4.3 Thermal Properties: Heat Transmission

In glass, heat is essentially transmitted through conduction and thermal radiation. Both its conduction and thermal radiation are measured by coefficients that are characteristic of the material—thermal conductivity, λ_C, and conductivity for radiation, λ_r, respectively. The sum of both coefficients provides the effective thermal conductivity.

When a heat flow passes through a sheet of glass with a thickness of d, through a surface S, the amount of heat that passes through the glass (Q), in the time period t, for a temperature gradient $T_1 - T_2$ between both surfaces of the glass, is shown by the equation:

$$Q = -\lambda_c S \frac{T_1 - T_2}{d} t \tag{8.15}$$

The minus sign shows that the direction of the heat flow is against the temperature increase. The thermal conductivity of glass depends on the composition and is found in the interval 2.90–3.60 kW/m/K.

At temperatures below 200 °C, heat transmission in glass is almost exclusively through conduction. The conduction coefficient increases with temperature, although it does so in progressively smaller increments, becoming practically constant for temperatures over 900 °C.

Over 550 °C, the mechanism of transmission is replaced with thermal radiation, which predominates above 1,000 °C.

For a given wavelength (or for an interval of wavelengths where the wavelength absorption coefficient, ε, is constant), the heat transfer coefficient is calculated by:

$$\lambda_r = \frac{16\sigma n^2 T^3}{3\varepsilon} \tag{8.16}$$

where n is the refractive index for the glass and σ the radiation constant equal to 5.746×10^{-12} J/s/cm^2/K^4.

Double glazing improves heat insulation with a gap (usually filled with air) between the glass panels. Thermal insulation is quantified by U, a calculation of the rate of heat loss through a material. A piece of *ordinary glass* has $U \sim 5.7$ W/m^2 K, and *double glazing* (with panels of ordinary glass) has $U \sim 2.5$–3.5 W/m^2 K.

In *double glazing*, the heat passes through the gap between the glass through conduction, convection and radiation. For *double glazing*, formed out of two panels of ordinary glass with a 12 mm air box, the speed of heat transfer is approximately the same for the three mechanisms.

The amount of heat transferred through conduction can be reduced by increasing the thickness of the air box in the *double glazing*. In contrast, the amount of heat transmitted through convection is reduced by reducing the thickness. Thermal insulation in *double glazing* is thus optimised by the space in between the two panes of glass ~16 mm thick.

In *double glazing*, the balance between conduction and convection can also be affected by the choice of gas used to fill the gap. Replacing the air with argon reduces U by between 0.15 and 0.4 W/m^2 K. A vacuum is better than any gas. In this case, the difficulty is in choosing a sealant that is effective at atmospheric pressure.

Heat transfer by radiation does not depend on the gas in between the glass panels. The amount of heat transferred by radiation does not depend on what is filling the gap or the thickness of the box—it only depends on the emissivity of the glass surfaces. Emissivity is a property of the material's surface that measures its capacity for absorbing or emitting electromagnetic radiation (light, colour), on a scale of 0–1. For any material, emissivity can change depending on radiation wavelength. Materials with low emissivity within the visible wavelengths create good mirrors—the light reflects the whole surface. Metals have low emissivities (emissivity ≤ 0.02). The vast majority of materials present high emissivity, around 0.9. *Coated glass* with an emissivity below 0.2 is defined as a *low-emission glass or low-E glass*.

A coating that contains silver nanoparticles can provide emissivity of between 0.02 and 0.12. Using glass with this sort of coating, in *double glazing*, can effectively reduce the radioactive component of heat transfer from the gap in the *double glazing*, reducing U by ~40 %.

8.5 Corrosion

The high resistance of glass to corrosion is due to the high chemical stability of the structure combined with a lack of grain limits. Because of this, glass is considered to be a (chemically) inert material.

But in practice, no material is chemically inert. In glass, although the mechanisms of chemical degradation are sometimes hard to establish, knowledge of the chemical composition of glass and the environmental conditions it will be subjected to are essential. In architecture, situations where it is exposed to highly reactive chemical solutions, as is the case in pipelines, containers with chemical products or even the packaging of some food products are excluded. However, in acid rain and warm salt-water environments (for example in aquariums), the contact with chemical products used for sealants or for the assembly of the windows with other building materials, along with the use of unsuitable cleaning products, are relatively common situations.

Chemical attack on glass occurs with two different mechanisms that can occur simultaneously: etching and leaching.

8.5.1 Etching

E*tching* is characteristic of an alkaline attack. In the initial stage, a gel forms on the surface of the glass, due to physical water adsorption. The absorbed water starts to chemically attack the silicate by breaking up the siloxane bonds as shown:

$$\equiv \mathrm{Si}-\mathrm{O}-\mathrm{Si}\equiv +\mathrm{H}^{+}+\mathrm{OH}^{-}\rightarrow\equiv \mathrm{Si}-\mathrm{OH}+\mathrm{HO}-\mathrm{Si}\equiv \tag{8.17}$$

The silica is gradually destroyed and silicic acid is produced, $\mathrm{Si(OH)_4}$.

Alongside with the attack on the protons, groups of hydroxyls attack according to:

$$\equiv \mathrm{Si}-\mathrm{O}-\mathrm{Si}\equiv +\mathrm{OH}^{-}\rightarrow\equiv \mathrm{Si}-\mathrm{OH}+\equiv \mathrm{Si}-\mathrm{O} \tag{8.18}$$

The non-saturated $\equiv$Si–O^{-} groups can react with water molecules and form new silanol groups OH^{-}, as shown in:

$$\equiv \mathrm{Si}-\mathrm{O}^{-}+\mathrm{H_2O}\rightarrow\equiv \mathrm{Si}-\mathrm{OH}+\mathrm{OH}^{-} \qquad (8.19])$$

As the silica network is destroyed, the remaining components in the glass are released whilst the glass is partially dissolved.

Assuming that a deposit of reaction products does not form on the surface and that the concentration of the solution remains the same, the corrosion continues at a constant speed. The temperature and speed of corrosion is measured using the Arrhenius equation:

$$\log Q = C/T \tag{8.20]}$$

where Q is the speed of corrosion, T is absolute temperature and C is a constant of the process. For every 10 °C increase, the speed of the corrosion reaction in an alkaline medium will double.

In most *etching* situations, deposits are not formed on the surface as it is kept clean. However, if the chemical attack was selective or if a deposit formed, the surface will remain uneven and rough to the touch. The accumulation (adhesion) of reactive produces on the surface, like silica or reactive insoluble products, makes it hard to monitor the corrosion process.

Alkaline chemical attack is sensitive to pH levels, increasing the reaction speed for every pH unit. The surface of the glass is hydrophilic and water is an aggressive agent. But water attack is minimal compared to alkaline attack. When water wets the surface of a glass with a crack, the energy in the surface of the glass decreases so the energy needed to spread the crack is reduced. The amount of water can be an important variable when it comes to the speed at which cracks spread.

8.5.2 Leaching

Predominantly in acid environment, the leaching is a process of ionic exchange, with selective removal of the soluble components of glass (Fig. 8.22). Here the process is controlled by diffusion, involving the permutation of hydrogen ions, in

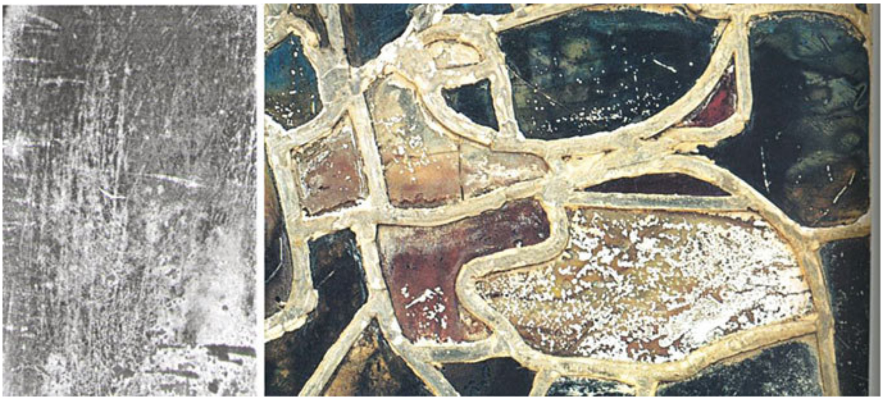


Fig. 8.22 Secondary corrosion: risks and stings in a mediaeval glass from Mosteiro da Batalha (Courtesy of Dr. Pedro Redol, Director of Mosteiro da Batalha, Portugal)

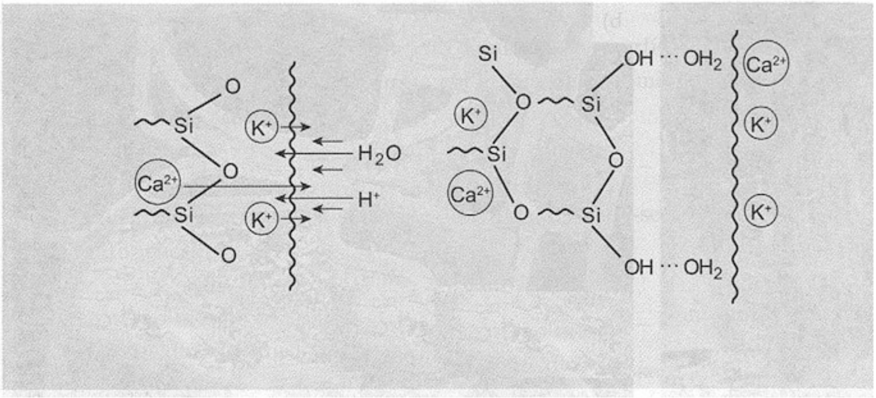


Fig. 8.23 Leaching of a silica-modified glass

the solution, with alkaline ions in the glass. The attack is generally selective, with the network cation modifiers:

$$\equiv \mathrm{Si} - \mathrm{O}^{-}\mathrm{Na}^{+} + \mathrm{H}^{+} + \mathrm{OH}^{-} \rightarrow \equiv \mathrm{Si} - \mathrm{OH} + \mathrm{NaOH} \qquad (8.21])$$

The silica network remains intact, however, whilst the ion modifiers are leached. As in the basic attack, the speed of corrosion follows the Arrhenius equation, doubling for every increase by 10 °C.

Corrosion by leaching leads to the formation of a surface deposit enriched with silica (Fig. 8.23). When the deposit reaches 0.1 μm, there is interference with reflected light. Deposits that are over 0.1 μm thick create iridescence and microcracks or break down the glass. However, the formation of these deposits can even improve the chemical resistance of the glass to corrosion as they act as a protective barrier and make diffusion more difficult—one of these examples is that of ancient Roman glass (Fig. 8.24).

With an acid attack, the pH effect is not relevant as in basic attack. pH of 1 is only a little more corrosive than a pH of 6. The speed of acid corrosion is still much slower than the speed of basic corrosion.

A process of corrosion, besides changes in chemical compositions, can lead to surface microporosity of around 1–10 μm or the formation of microcracks. In extreme cases, a leached glass surface can break or damage the surface structure. In these cases, the glass will take on a smoky appearance and a surface deposit or microcracks may become visible.

Glass that has been strengthened with *heat treatments* or *tempering* develops greater resistance to chemical corrosion; those that have been excessively annealed become thick and susceptible to corrosion.

For glass with surface coatings, these coatings should be viewed as potential contaminating agents after chemical attack.

The chemical composition of glass determines its resistance to corrosion. Depending on the acid attack, the greatest resistance to corrosion is found in pure silica glass, where there are no modifiers. As the level of modifiers increases and the

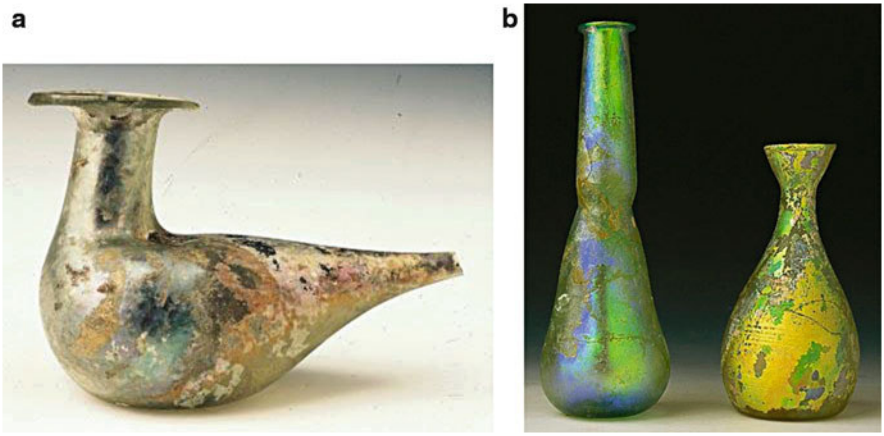


Fig. 8.24 Iridescence in Roman glasses

network becomes more open, vulnerability to corrosion increases. The presence of alkaline-earth oxides or the presence of large cations restricts mobility within the glass network and improves resistance to corrosion.

8.6 Conservation, Durability and Cleaning

8.6.1 Condensation

Condensation often occurs on glass and mirror surfaces. When water vapour inside a room remains in contact with a window surface, and dew point temperature is reached, then the vapour condenses into droplets. This is what can be found, for example, on a mirror or on bathroom walls after a hot shower. Condensation can also occur inside windows if temperatures of the inner surface are much higher than the outer surface.

The variables that affect condensation inside the windows of a room are: (1) temperature of the outer surface of the glass, (2) temperature of the inner surface of the glass, (3) relative indoor humidity and (4) natural ventilation of the house.

8.6.2 Removing Condensation from Inside Windows

Using *double glazing*, in frames with a thermal break, is mandatory for avoiding condensation. In *double glazing*, if possible use *low-E glass* to reduce the temperature gradient between the inner and outer glass.

Keep the level of relative humidity inside the room at around 30–50 %.

Keep the level of ventilation in the house high (check extraction units; get the level of forced ventilation right; open windows on a daily basis, even if it is just for short periods; and air out basements and attics each year).

8.6.3 Handling and Storage

There are specific recommendations for different types of glass for *storage* and *handling*.

8.6.4 Cleaning

Cleaning products used on glass should be chosen carefully (see *Corrosion*). It should be highlighted that the chemical composition of the surface of glass can be very different to its inner composition, due, for example, to the presence of surface coatings (see *Anti-reflection Glass and Low-Emission Glass*) or by the fact that chemical degradation may have started (see *Corrosion*).

There are specific recommendations for different types of glass for *cleaning and maintenance*.

8.7 Recycling: Life Cycle

Glass is the only material that is 100 % recyclable! We should bear that in mind when facing a project, as sustainable development is only possible by careful use of resources and technology.

Implementing recycling management systems depends largely on government directives. For container glass, EU Directive 94/62/EC harmonises legal, regulatory and administrative legislation for the member states on packaging and packaging waste. The transposition into the Portuguese legal system is through Executive Law no. 322/95 and Ministerial Order no. 313/96. European Directive 94/63/EC proposes the principles of *prevention* (by reducing the amount of packaging waste produced), *reduction* (by encouraging reuse or recovery of waste), *responsibility* (making economic operators responsible for dealing with packaging waste) and *elimination* of trade barriers and free circulation of packaging within the European Union. The management of flat glass recycling, whether it is destined for use in residential building construction and architecture or the vehicle industry, is not regulated.

Glass made using cullet results in lower energy costs. From an environmental point of view, the extraction of raw materials is reduced, gas emissions during glass melting is minimised and the creation of municipal solid waste (MSW) is managed. For every tonne of glass recycled, the amount of raw materials needed is reduced by 120 kg, the fuel needed is reduced to 130 kg and MSW is reduced by 1,000 kg.

In flat glass production, due to the high-quality raw materials needed, recycling is limited to rejects from the factory production line (industrial cullet). Although glass is always recyclable, the recycled artefact produced is gradually contaminated, turning into a brownish green, making it unsuitable for use in architecture and the building industry. This is the reason why domestic cullet is forbidden in *float* glass factories.

Processed *float glass* is also problematic when it comes to recycling with laminated glass, for example, the layers of polymers contaminate the production process; in *coated glass* (*mirror glass*, *low-emission glass*, etc.), the films on the surface contaminate the glass. Glass with defects (stones, devitrification, etc.) cannot be used in the glass production process.

Glass that cannot be reused in the productive process can be used in other products as an inert material.

Environmental Factors

Raw materials	Silicon oxide (SiO_2) is one of the main components of the Earth's crust (75 % of its mass)
Extraction	Changing the landscape
Energy	Intensive energy use
Safety	Low chance of toxic metals
Recycling	*100 % recyclable*

8.8 Glasses Used in Construction and Architecture

In projects, thickness should be calculated, whether for simple glass (ordinary glass, silk*screen printed glass*, *rolled plate glass*, *anti-reflection glass*, *mirror glass*, *low-E* glass, *self-cleaning glass*, *tempered glass*) or composite glass (*laminated glass*, double glazing), using software provided by the manufacturer. These programmes optimise the optical and heat performance.

8.8.1 Ordinary Glass (*Clear Float Glass*)

Simply annealed glass is the easiest flat glass to manufacture. It can be coloured or colourless. The majority of *float glass* is just annealed glass—referred to here as *ordinary glass*.

How It Is Produced

To produce *ordinary glass*, a *float* process is used.

Where It Should Be Used

Ordinary glass was traditionally used in windows and openings in rural and urban dwellings. Nowadays, more efficient solutions are sought to tackle the problems of heat and sound insulation, as well as optimising lighting conditions in buildings and housing.

Ordinary glass is often damaged and weakened by *corrosion*. When carrying out renovation work, *double glazing* is often recommended.

Table 8.2 Standard sizes of *float* glass

Thickness (mm)	Width (mm)	Length (mm)
2.1	2,520	
2.3	2,700	
2.6	2,900	
2.85	2,920	
2.90	2,960	Until
3.15	2,980	6,000
3.50	3,000	
3.85	3,020	
3.90	3,030	
4.85	3,050	
4.90	3,060	
5.85	3,100	
5.90	3,120	
8	3,150	
10	3,180	
	3,200	
	3,210	
	3,300	

Table 8.3 Dimensional tolerance for *float* glass (ASTM C1036)

Thickness		Range of tolerance	
Denomination (mm)		Min. (mm)	Max. (mm)
1.0	Micro-*slide*	0.79	1.24
1.5	Photo	1.27	1.78
2.0	Square	1.80	2.13
2.5	Simple	2.16	2.57
2.7	Laminated	2.59	2.90
3.0	Double–1/8″	2.92	3.40
4.0	5/32″	3.78	4.19
5.0	3/16″	4.57	5.05
5.5	7.32″	5.08	5.54
6.0	1/4″	5.56	6.20
8.0	5/16″	7.42	8.43
10.0	3/8″	9.02	10.31
12.0	1/2″	11.91	13.49
16.0	5/8″	15.09	16.66
19.0	3/4″	18.26	19.84
22.0	7/8″	21.44	23.01
25.0	1″	24.61	26.19
32.0	1-1/4″	28.58	34.93

Recommendations for All Glass Types

- Storage
  In the storage facility, always avoid contact between two glass panels. There is a possibility of chemical and/or mechanical damage due to acid attack (see

Corrosion). All types of glass should have sheets of paper or flexible spacers between them to keep them separate.

- Handling
  Glass is a fragile material so it should be handled with care.
- Cleaning
  Hydrofluoric acid solutions or other fluoride compounds should not be used around any glass surface.
- Note
  Standard sizes can vary a little from one manufacturer to another. *Float* glass can also be produced to a size that is not considered standard. Check with the manufacturer before approving the project.

8.8.2 Decorated Glass

Decorated glass—*silkscreen printed glass* or *rolled plate glass*—enables light transmission to be controlled, reduces the absorption of solar energy and can create different environments, with or without visibility, defining levels of privacy.

8.8.2.1 Silkscreen Printed Glass

Silkscreen printed glass is a *float* glass decorated by screen printing.

How It Is Produced

Silkscreen printed glass is decorated using a screen printing technique. The frit is applied using screen printing in three distinct patterns—dots, lines, empty gaps or across the whole surface. Depending on the pattern, the end product can be transparent, translucent or opaque. The combination of a large range of basic glass and a huge range of frit colours offers designers great creative flexibility.

Silkscreen printed glass is longer lasting than glass decorated using chemicals or sand baths. *Silkscreen printed glass* is heat treated to reduce the risks of cracking when exposed to the sun for long periods of time.

Where It Should Be Used

Silkscreen printed glass is designed to be used indoors, for example, in doors, screens, decorative ceilings, bathrooms, shower cabinets, lift walls and hotel awnings. Designed for enclosed or open spaces, *silkscreen printed glass* is easy to clean and *graffiti* resistant.

When *coated*, *silkscreen printed glass* can be used outdoors.

Specific Recommendations for Silkscreen Printed Glass

- Storage
  The silkscreen printed surface should be coated.

8.8.2.2 Rolled Plate Glass

Rolled plate glass is a clear, colourless or coloured glass with a design printed on one side.

How It Is Produced

Rolled plate glass is produced by stretching and rolling the glass after it is produced (*offline*). When it is rolled, a motif is pressed on using one of the rollers.

Where It Should Be Used

Rolled plate glass is designed for indoor, such as in doors, screens and urban furniture.

Rolled plate glass can be wired, i.e. during the rolling process, a metal netting is applied to the glass which makes it more resistant and retains the glass pieces if it breaks whilst stopping people from breaking through it.

Specific Recommendations for Rolled Plate Glass

- Use in Construction
  Rolled plate glass features a pattern. This has an aesthetic effect, so when it is assembled, the cut pieces need to be placed so they are aligned and facing in the same direction.
- Note
  Rolled plate glass cannot be laminated.

8.8.3 Coated Glass

The term *coated glass* coves any type of glass (*ordinary* or *tempered*) to which a coating has been applied. The coatings most common in *float* glass are metallic films and metal oxide films. The term *coated glass* does not include varnish.

Coated glass can be divided into two main categories—*coating* during the production process (*online coating*) and *coating* after the production process (*offline coating*).

In *offline* coated glass, the coating is applied by chemically polishing the surface using acids or pyrolysis. All these methods were developed in the 1960s and can be applied to glass that has been previously treated with heat or temper.

The coatings applied during the *float* process emerged in the 1970s—the coating occurs inside the bath used in the *float* glass process. Placing *sputtering* units (thermal evaporation) at the end of the *float chamber* allows the glass to be coated with different materials, before annealing. Deposition takes place at high temperatures (~600 °C) and creates tough and durable coatings, whilst in use, at room temperature. After coating, the glass can be tempered.

The colour of the coated glass is not due to the colour of the film coating but due to the constructive interference caused by the layers of film deposited (Fig. 8.17).

Glass with different levels of solar control can be produced by controlling the composition and thickness of the film deposited.

8.8.3.1 Anti-reflection Glass

Anti-reflection glass is a glass with a special surface coating that has specific optical properties. *Anti-reflection glass* allows the light reflective components to be minimised and the transmission component to be maximised so that transparency and visibility in transmission are optimised.

Through the chemical composition of the coating, it is possible to control the levels of glass transmission, tunning visibility along with IV and UV reflectivity.

Where It Should Be Used

High transmission makes *anti-reflection glass* suitable for use in displays and show windows, in commercial and museum settings.

Anti-reflection glass is also used to produce *double glazing*, outdoors, with the coated surface placed on the outside of the *double glazing*.

8.8.3.2 Mirror Glass

Mirror glass is a glass with a special coating that has specific optical and thermal properties. *Mirror glass* maximised the light reflection and minimises light transmission.

Where It Should Be Used

Mirror glass is also used in *double glazing*, outdoors, with the coated surface placed on the outside of the *double glazing*. *Mirror glass* is used for the outdoor surfaces of buildings.

8.8.3.3 Low-Emission Glass

Low-emission glass is a glass where one of the surfaces is coated with an invisible metallic film that reflects UV radiation. The film coating can be applied using pyrolysis or vacuum deposition. Cobalt oxide and chrome oxide are used for coating *low-emission glass*. Indian oxide and titanium oxide reflect UV radiation whilst remaining transparent for visibility, so they are also used in *low-emission glass*.

Copper, aluminium and nickel oxides are used for indoor coatings, as the coatings are less durable.

Low-emission glass is a glass that increases energy efficiency in a building as it reduces the transfer of heat from inside to outside (it is usually used in *double glazing* or *coated glass*).

Table 8.4 *Standard* optical performance[a]

						U		U (European)	Solar coef.
Thickness	Visible		E. total		UV	Summer	Winter		
(mm)	% *T*	% *R*	% *T*	% *R*	%*T*	air	air	air	
2.5	64	10	48	13	51	0.69	0.75	3.7	0.55
3	65	10	48	12	49	0.69	0.75	3.7	0.55
4	64	10	47	12	46	0.69	0.75	3.6	0.54
5	62	10	46	12	45	0.69	0.75	3.6	0.53
6	61	10	44	11	43	0.69	0.75	3.6	0.52

[a] Characteristic values may depend on the manufacturer

Where It Should Be Used

Low-emission glass is also used in *double glazing*, with the coated surface placed on the inside of the *double glazing*.

Low-emission glass, when used in *double glazing* or *coated glass*, easily brings high thermal comfort levels. It is recommended for use in public buildings, such as hospitals, schools, offices, shops or homes.

- Beware!

  There may be legal restrictions for using *mirror glass* on the outside of buildings. In some places where there is high solar radiation, councils place a maximum limit on reflective coatings on buildings. In urban environments, a highly reflective coating can significantly increase the energy costs of air conditioning in surrounding buildings.

  Designers can always use high absorption glass to achieve the right energy balance.

Recommendations for Coated Glass

- Storage

  There are limits to how long you can store glass with special coating. Check with the manufacturer!
- Handling

  Manual or other types of handling should be carried out using lint-free soft cotton gloves that are low friction. Do not use paper gloves.

  For machine handling, place a thin, smooth sheet of paper between the glass coating and the mount.
- Cutting

  The glass should be placed on the cutting table with the coated surface face up.

  Cutting should be carried out on the coated surface when dry. Never use water as a lubricant, as it can chemically react with the film coating or the freshly cut surface (see *Corrosion*). If necessary, use oil-based lubricant, but never too much.

  The glass shards should be cleaned up using dry compressed air.
- Washing

  The glass should be regularly cleaned after it has been fitted.

  An automatic washing machine should be used for washing *coated glass* (rotating brush and fast drying).

8.8.4 Self-Cleaning Glass

Self-cleaning glass is a self-sufficient glass when it comes to cleaning and reduces the cost of building maintenance.

Self-cleaning glass is a glass with a surface coating having hydrophilic or photocatalytic properties.

- Hydrophilic surface coating

  Self-cleaning glass is coated with a hydrophilic film. The hydrophilic nature changes the angle between the drop of water and the glass from 30–40° to 4°–7°, so a thinner water film forms on the glass. Raindrops spread out easily and evenly on the glass surface without leaving marks from the run off. The reduced thickness of the water film allows it to dry faster. Both effects reduce the level of residual minerals left on the glass.
- Photocatalytic surface coating

  Self-cleaning glass is coated with a photocatalytic film. The film is generally made of titanium oxide; it is activated with UV radiation and oxygen released in a photocatalytic reaction, which gradually but continually breaks down the bonds in the organic compounds left on the glass. *Self-cleaning glass* is thus able to process the organic waste at the same time as it breaks away from the glass, making it easier to remove. The presence of a photocatalytic and hydrophilic film keeps the glass clean for longer (provided that it is exposed to both solar radiation and rainwater).

  The photocatalytic film is stable and resistant to oxidation, ensuring good performance over time.

Where It Should Be Used

Self-cleaning glass should be used on outer surfaces that are well exposed to the sun and in rainy climates (when it does not rain, water should be used to clean it to remove organic waste).

Self-cleaning glass can be used in *double glazing*, as the outer glass with the option of the second glass being *low-emission glass*.

Self-cleaning glass should always be used on the outside especially with *laminated glass* and *double glazing*.

Specific Recommendations for Self-Cleaning Glass

- Washing

  Each year, the surface of the *self-cleaning glass* should be cleaned. The frequency of this cleaning depends on the outdoor conditions (i.e. position in relation to the sun, intensity of UV radiation, annual rainfall).

  An automatic washing machine specifically for washing coated glass (rotating brush and fast drying) should be used.

  For automatic washing machines, polypropylene is recommended and nylon® brushes are not advised (polypropylene has a lower friction coefficient and is softer and more flexible than nylon®).

  It is recommended that brushes are used for cleaning to avoid using abrasive materials on the glass.

  Dry air should be filtered (to avoid leaving water marks on the surface of the glass).

  For manual washing, a liquid soap or other washing fluid should be used. It should be dried using soft paper to prevent leaving marks on the photocatalytic coating. The drying process should stop when there is still a thin film of water on the surface.

Check with the manufacturer to find out what temperature water should be used to wash it.

Check with the manufacturer to find out if purified water should be used for the final rinse.

- Note
  The inner surface of *self-cleaning glass*, which is not coated in photocatalytic film, should be washed regularly.

  It is possible that the photocatalytic effect can be impaired by an unusually high build up of organic or non-organic materials on the glass, deposited, for example, by rain water.
- Use in Building
  Check with the manufacturer whether the photocatalytic coating needs to be activated. If it does, expose the glass to solar radiation for 48 h (in the northern hemisphere, it should be facing south to optimise UV exposure). Check that the coated surface is facing the sun. If the weather is not suitable, increase the length of time for which it is exposed to the sun. To check that the photocatalytic film has been activated, pour water over the surface and check to see if it spreads out forming an even and unbroken film (not forming drops). If it does, the film has been activated.

  The glass should be set in place immediately after the photocatalytic film has been activated. If it is not, then it may be necessary to repeat the activation process.

  After activating the photocatalytic coating, do not wash the glass.

  The surface of *self-cleaning glass* should be protected from sealants. Sealants that are based on polyurethane, polysulphate, etc. may temporarily affect the hydrophilic nature of the coating. Silicon-based sealants may affect the photocatalytic nature of the coating several centimetres from the point of contact.

  Neoprene- or butyl-based glazing tape contains a high level of oils that are hard to remove from the glass surface.
- Beware!
  Sharp objects, steel wool and acid, basic or abrasive detergents are not allowed on the coated surface of the glass.

8.8.5 Safety Glass

Safety glass is understood to be a glass with safety performance that protects goods, spaces or people. This category includes *laminated glass* and *tempered glass*.

8.8.5.1 Laminated Glass

Laminated glass was first sold commercially in 1910. A sheet of polymeric material is placed between two glass plates, and they are heated until the polymeric material binds to the inner surface of the glass panels. The polymeric sheet first used was based on biodegradable celluloid and makes the *laminated glass* quite susceptible to hydrolytic attack. The use of *laminated glass* in vehicle windscreens was then replaced by *tempered glass*, in the 1930s, which is chemically inert when in contact with water. It was only in the 1950s that PVB had started to be used and *laminated glass* remained in use in the industrial vehicle industry. In the 1960s, *laminated glass* became the preferred choice for vehicle windows, and in the 1970s, it was started to be used in buildings. PVB can be replaced by polyurethane, EVA or CIP (SentryGlasPlus®), polymer materials that give *laminated glass* better mechanical performance although with higher production costs.

How It Is Produced

Laminated glass has two (or more) sheets of glass that is joined by one (or more) synthetic film coating(s) of PVB. After the polymeric film is placed between two sheets of glass, the composite is introduced in an autoclave, where the heat treatment under pressure helps it to stick. Once sealed, the resulting material (a sandwich of glass and PVB) behaves as one complete unit and looks like a single piece of glass.

Ordinary or *tempered glass*, as well as *coloured glass* or *white glass*, *low-E* or *anti-reflection glass*, can be used to produce *laminated glass*. The sheet (or sheets) of PVB can be colourless, opaque or coloured. The number and thickness of each one of the parts can vary. The combination of a wide range of glass and PVB films offers a large flexibility in projects with *laminated glass*. An assemblage of *laminated glass* with multiple sheets of glass joined with various PVB films offers increased safety and protection.

Beware! Mechanical performance of the PVB synthetic film is only stable between the temperature range of 10 °C and 45°C!

Where It Should Be Used

Nowadays, *laminated glass* is considered to be the best choice for external cladding on buildings. It is difficult to harmonise in a single material a high-quality finish, transparency, light and solar control, thermal and/or sound insulation, protection against cyclones, wind or even explosions, bullets or missiles. *Laminated glass* is no more resistant to breakage than *annealed glass*. Although, in the case of an impact, the PVB film is able to absorb the mechanical energy, the material resistance of *laminated glass* is increased a lot. And, if broken, the PVB film retains glass fragments, preventing them from dropping out and potentially causing an accident, whilst they continue to act as a barrier against people or objects.

After breaking, *laminated glass* continues to prevent people or objects from getting in, with the pieces of glass held in the support or frame.

It is also hard to beat its resistance to corrosion in urban environments (except in some industrial environments).

Apart from high performance and multifunctionality, *laminated glass* is very durable, preserving the aesthetic side of the glass. *Laminated glass* offers a combination of solutions to many of the problems in architectural projects whilst offering protection.

Laminated glass can be designed to satisfy the most demanding project requirements. Some typical thicknesses of laminated glass are 6.4 mm (3|0.46|3), 8.8 mm (4|0.76|4), 10.8 mm (5|0.76|5) and 11.5 mm (5|1.52||5).

Properties of Laminated Glass

- Note

  All glass can be *laminated* with the exception of *rolled plate glass*.
- Safety

  Laminated glass meets all the safety requirements for glass, for vertical or oblique use or as roofing. If it breaks, the glass pieces stick to the PVB preventing accidents involving people or property, continuing to provide a barrier against penetration; thus *laminated glass* offers a series of advantages compared to *tempered glass*. *Laminated glass* is often used in halls and skylights in hotels and public galleries.

  Laminated glass, although it breaks more easily than *tempered glass*, continues to act as a barrier to prevent people or objects getting through. However, *laminated glass* breaks in a star pattern and in sharp pieces unlike *tempered glass*, which breaks into small pieces with no sharp edges.
- Protection

  Laminated glass offers more protection for people and property than other types of glass. *Standard laminated glass* (two glass sheets) is enough to protect against forced entry. In multilayered pieces or where the thickness of the PVB film is double or triple than *standard* one, *laminated glass* can even resist projectiles, heavy objects or small explosions. Normally various projectiles hitting in the same pattern are needed to break through it. The thickness of *laminated glass* offers between 2.5 and 7.62 cm in protection, depending on the calibre of what it is trying to resist.

  Laminated glass is recommended in police or army barracks, courts, high-security courtrooms, banks, insurance companies and pharmacies.
- Sound Control

  Laminated glass is efficient for providing sound insulation in commercial and residential properties and particularly in television sound studios. The acoustics of *laminated glass* are due to high sound absorption by the PVB. Where even higher performance is needed, *laminated glass* can be produced with several sheets of glass composed with multiple PVB film coatings.

  Laminated glass is currently used in airports, museums, sound studios and schools with the aim of insulating against unwanted noise from planes, heavy machinery, traffic or other factors.

  The ASTM standards define a sound transmission classification (STC). STC is a number calculated from individual transmission loss at specific test frequencies (ASTM E 90 and ASTM E 413). The higher the STC rating, the greater the reduction in sound.
- Sound and UV Filter Control

Solar energy is turned into heat energy when it is absorbed. In many buildings, the primary goal is energy control. This objective requires coating surfaces with a material that can reflect and absorb and reemit solar energy.

Transmission, reflection and light and energy absorption are factors that depend on the colour of the PVB. *Laminated glass* is an efficient filter of UV radiation (~95 %). That is why it protects against decolouration and deterioration of materials caused by UV radiation and is especially useful in shop windows.

- Energy Control

  The heat transfer coefficient of *laminated glass* is similar to *simple glass* of the same thickness.

  For greater heat performance, a combination of *low-emission glass* with *laminated glass is recommended.*
- Natural Hazards and Explosion

  Laminated glass has a key role in protecting against accidents. Adhesion between the glass and the PVB helps prevent accidents caused by falling pieces of glass.
- Glass Fitted Vertically, Obliquely or as Roofing

  Glass fitted at more than a 15° angle is considered oblique glass. *Laminated glass* is recommended for oblique or roof fitting, as after breaking the glass remains in the PVB.

Specific Recommendations for Laminated Glass

- Handling

  The edges of *laminated glass* should be handled with care, avoiding contact with water or organic solvents. Exposure to water can cause the glass to become opaque or even wear away the laminate, so it is essential that the edges are well protected whilst it is stored and fitted.
- Compatibility

  All *laminated glass* contains polymers. That is why solvents, acids or alcohol solutions that are present in insulation tape and sealants can chemically react with the organic components of the *laminated glass*. Most sealants used on glass react chemically with the polymeric materials. Compatibility should not be assumed.

  Sealant manufacturers should produce reports showing the test results for compatibility between *laminated glass* and insulating materials with silicon, painted or anodised aluminium, insulation tape, masonry, etc. Silicon, which is commonly used as a sealant, in contact with PVB can wear away the laminate up to 50 mm in depth.
- Assemblage/Use in Building

  Laminated glass can be produced to suit the project requirements, in terms of the size, type of glass or PVB. *Laminated glass* can also be used as a monolith or in double glazing. *Laminated glass* can be cut or drilled during the building process unlike *tempered glass*.

  Laminated glass should be sealed to avoid any potential condensation or humidity inside. Inside the frame of the *laminated glass*, there should be at least three holes (each 5 mm) that allow rainwater or condensation to drain quickly.

Prolonged exposure of the laminated surface to humidity can lead to nebulosity or wear off the laminate from the surface. When fitting, more elastic sealants are recommended, such as silicon, polyethylene foam or chloroprene rubber.

Laminated glass can be cut during building work.

- Note

  Laminated glass performs well, particularly in terms of 'safety and protection', provided that a suitable frame is used (frame standards: prEN 1627-1, EN 1522 and EN 1523).

  European and North American standards for safety glass and protection: ASTM C1036, C1172, C1048, PR EN 356 (European Standard), CTK 4 Union Professionelle des Entreprises d'Assurance (UPEA or BVVO), CPSC 16CFR 1201ANSI Z-971 – 1984

Table 8.5 Standard dimensions of laminated glass

Glass composition	Standard thickness (mm)	Maximum dimensions (mm)
Ordinary glass + ordinary glass		
3 + 3	6.0	1.800 × 1,200
5 + 5	10.0	
6 + 6	12.0	2.800 × 2,000
8 + 8	16.0	
10 + 10	20.0	3.500 × 2,500
12 + 12	24.0	
15 + 15	30.0	
5 + 6.8	11.8	
6 + 6.8	12.8	2.400 × 1,800
8 + 6.8	14.8	
8 + 10	18.0	
10 + 10	20.0	3.500 × 2,400
12 + 10	22.0	
Anti-reflection + ordinary glass		
6 + 6	12.0	2.400 × 1,800
8 + 8	16.0	
10 + 10	20.0	
12 + 12	24.0	3.500 × 2,400
Tempered + ordinary glass		
5 + 5	10.0	2.400 × 1,800
6 + 6	12.0	
8 + 8	16.0	
10 + 10	20.0	
12 + 12	24.0	
15 + 15	30.0	3.500 × 2,400

[a] Standard dimensions may depend on the manufacturer

Table 8.6 Security glass/protection classes EN356

(EN 356 'classes in construction—security glass—tests and rating for resistance to manual attack') tests	Performance	Class	Level
Fall of 3 bols, height 1.5 m	Uncrossed	P1A	1°
Fall of 3 bols, height 3 m	Uncrossed	P2A	1°
Fall of 3 bols, height 6 m	Uncrossed	P3A	1°
Fall of 3 bols, height 9 m	Uncrossed	P4A	1°
Fall of 9 bols, height 9 m	Uncrossed	P5A	2°
Mass + Ax 30 blow	Manway not held	P6B	2°
Mass + Ax 51 blow		P7B	2°
Mass + Ax 71 blow		P8B	2°

Note: Test sample, glass plate 110 cm × 90 cm, horizontally positioned. Bols of 4.1 kg. After the third impact the glass must not fracture. Machetes perform an opening of 40 cm × 40 cm, designated by 'manway'

Table 8.7 Security glass/protection classes EN 1063

Type of gun	Calibre	Type	Mass (g)	Gunshot (m)	Speed (m/s)* gunshot	Class EN 1063
Shotgun/carbine	0.22 LR	L/RN	2.6 ± 0.1	10 ± 0.5	360 ± 10	BR1-S
Shotgun/carbine	0.22 LR	L/RN	2.6 ± 0.1	10 ± 0.5	360 ± 10	BR1-NS
Pistol	9 mm automatic	FJ/RN/SC	8 ± 0.1	5 ± 0.5	400 ± 10	BR2-S
Pistol	9 mm automatic	FJ/RN/SC	8 ± 0.1	5 ± 0.5	400 ± 10	BR2-NS
Pistol	0.357 Magno	FJ/CB/SC	10.2 ± 0.1	5 ± 0.5	430 ± 10	BR3-S
Pistol	0.357 Magno	FJ/CB/SC	10.2 ± 0.1	5 ± 0.5	430 ± 10	BR3-NS
Pistol	0.44 R. Mag.	FJ/RN/SC	15.6 ± 0.1	5 ± 0.5	440 ± 10	BR4-S
Pistol	0.44 R. Mag	FJ/RN/SC	15.6 ± 0.1	5 ± 0.5	440 ± 10	BR4-NS
Pistol	0.44 R. Mag	FJ/RN/SC	15.6 ± 0.1	5 ± 0.5	440 ± 10	BR4-NS
Shotgun/carbine	5.56 × 45	FJ/PB/SCP1	4 ± 0.1	10 ± 0.5	950 ± 10	BR5-S
Shotgun/carbine	5.56 × 45	FJ/PB/SCP1	4 ± 0.1	10 ± 0.5	950 ± 10	BR5-NS
Shotgun/carbine	7.62 × 51	FJ/PB/SC	9.5 ± 0.1	10 ± 0.5	830 ± 10	BR6-S
Shotgun/carbine	7.62 × 51	FJ/PB/SC	9.5 ± 0.1	10 ± 0.5	830 ± 10	BR6-NS
Shotgun/carbine	7.62 × 51	FJ/PB/HC1	9.8 ± 0.1	10 ± 0.5	820 ± 10	BR7-S
Shotgun/carbine	7.62 × 51	FJ/PB/HC1	9.8 ± 0.1	10 ± 0.5	820 ± 10	BR7-NS
Shotgun	12/70	Brenneke	31 ± 0.5	10 ± 0.5	420 ± 20	SG1-S
Shotgun	12/70	Brenneke	31 ± 0.5	10 ± 0.5	420 ± 20	SG1-NS
Shotgun	12/70	Brenneke	31 ± 0.5	10 ± 0.5	420 ± 20	SG2-S
Shotgun	12/70	Brenneke	31 ± 0.5	10 ± 0.5	420 ± 20	SG2-NS

Note: Specimen, 110 cm × 90 cm piece of glass positioned horizontally. 4.1 kg test balls. On the third impact, the glass should not break. It can be struck with an axe to create a 40 cm × 40 cm opening for a person to get through

- Three impacts with the exception of SG1-S and SG1-NS, which involves just one impact
- *Key*: *L* lead, *CB* cannon ball, *FJ* metal coated bullet, *FN* cylindrical/conical truncated bullet, *HC1* steel centre ($m = 3.7 \pm 0.1$ g), *PB* cylindrical/conical bullet, *RN* cylindrical bullet/warhead, *SC* lead centre, *SCP1* steel coated lead centre

8.8.5.2 Tempered Glass

Although mediaeval manuscripts make reference to extremely mechanically durable glass, there is no proof that it existed. In 1870, in France, *tempered glass* was produced for the first time using vertical tempering in water. This glass was used in low-pressure viewfinders. In the 1930s, the first registered brand of tempered glass, Securit®, was marketed. The sheet of glass is supported by clamps on one of the edges and put into the furnace until it reaches a temperature of 600–640 °C. At this point, the glass is removed from the furnace and placed between two high-pressure air jets for thermal tempering. Over 500 °C, the glass becomes much less viscous so the marks from the clamps are left in the glass. *Tempered glass* is more mechanically resistant than annealed glass, and if it breaks, it does so in small pieces with *smooth edges*. This glass was an immediate success, and it has been used in the vehicle and construction industries and used in high standing buildings. In the 1970s, a horizontal tempering process was developed that did not leave clamp marks. Once this aesthetic issue was overcome, *tempered glass* became one of the first choices for public buildings and, in particular, for the restoration and conservation of historical or prestigious buildings, as long as frames were not required.

Tempered glass is a glass that has been chemically or thermally treated to improve its mechanical performance.[1] *Tempered glass* is two to five times more resistant than *annealed glass*. *Tempered glass* breaks into small harmless pieces, with edges that are not sharp, preventing people from getting injured.

How It Is Produced

Tempering can be thermal or chemical.

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[1] Glass breaks whenever the surface or edges are placed under a certain amount of tension. In these conditions, any slight crack on the surface or edges can spread to form visible damage.

The main principle behind tempering lies in creating a situation with initial compression of the surface or edges. This is achieved when the glass is reheated and rapidly cooled. In this way, the centre of the glass will remain warm compared to the surface, which will cool quickly. When the centre area of the glass cools, it compresses the surfaces and edges.

Wind pressure, the impact of a stone, heat tension or other applied forced can overcome this permanent surface tension and break it.

- Thermal Tempering

  Ordinary glass is given a thermal treatment where it is reheated until it is soft (~680 °**C** for soda-lime-silicate glass) and rapidly cooled.

  If rapidly cooled, the glass becomes four times more resistant than annealed glass (*ordinary glass*), and if it breaks, it does so in multiple pieces (with smooth surfaces). Minimum surface compression is 69 MPa. For the temper to be effective after breaking, the area of the ten biggest pieces of glass should be no more than 6.5 cm^2.

  If after the thermal treatment the cooling process is slow, the glass is only twice as strong as *ordinary glass*, and if it breaks, it does so in linear pieces, in a bigger area than *tempered glass*, but will still hold well in the support (thermally toughened glass). Surface compression is between 21 and 69 MPa.
- Chemical Tempering

  The cation exchange between lithium ions (Li^+), on the glass surface, and potassium ions (K^+) on the outside (immersion liquid), takes place by immersing the glass in a potassium nitrate solution for ~16 h at 400 °C. The exchange of lithium ions for potassium ions changes the chemical composition of the glass surface, and as the potassium ions are bigger than the lithium ions, it compresses the glass surface structure. The mechanical resistance of *tempered glass* chemically increases by five times compared to *ordinary glass*.

  Chemical tempering gives *ordinary glass* properties identical to those of glass that has been thermally tempered. Chemically *tempered glass* presents a surface compression between 45 and 69 MPa.

Where It Should Be Used

Thermally tempered glass is used for building fronts, sliding doors, entrance doors, museum exhibit cases, shower cubicles, stair gates, balconies or other uses where more resistance is needed. It can be used in the furniture industry and the electrical appliance industry or in fireguards. *Tempered glass* should be used whenever there is a chance of physical contact with the glass.

Chemically tempered glass is used for factory fittings where a finer strong glass is needed. Chemically tempered glass is mostly used in ophthalmic glass.

Tempered glass should not be used in situations where an explosion may occur (e.g. an explosion at a firewall).

Tempered glass should not be used to prevent forced entries or as a bullet shield. However, a combination of *tempered glass* and annealed glass (see *Laminated Glass* and *Double Glazing)* can be used.

For fireguards, the project should consider heat expansion as well as the thermal insulation of the sealants.

- Beware!

  Tempering creates permanent stress that can sometimes distort images reflected from certain angles. This is considered an intrinsic feature of *tempered glass* and not a defect.

The reflection or transmission of polarised light can create stress or iridescence. Again, this is considered an intrinsic feature of *tempered glass* and not a defect.

Tempered glass can also show signs of where it has been held by support grips (in vertical tempering) or a slight wave in the sheet from the rollers when produced using horizontal tempering.

Tempered glass is associated with a risk of serious breakage.[2] The project designer is responsible for the project specification for specific use.

Tempered glass used in *double glazing* and used above ground level should only be used as the inner layer of composite glass.

Specific Recommendations for Tempered Glass

- Handling
  The increased mechanical resistance of *tempered glass* leads to less care being taken when handling it, which could lead to damage to the edges. In this case, even low heat or mechanical stress can lead to a catastrophic fracture.
- Assembly/Use in Building
  Tempered glass cannot be cut or modified in any way after the thermal treatment. Perforation of the compressed surface layer causes the whole *tempered glass to break*.

Curved Tempered Glass

Curved tempered glass is a *tempered glass* that is not geometrically flat and can satisfy the project needs.

How It Is Produced

Curved tempered glass is a glass treated with a heat cycle *tempered glass* where the maximum temperature (~600 °C in soda-lime-silicates) is slightly lower than the softening temperature (~680 °C in sodium-calcium-silicates). The shape is created in a mould designed using CAD.

Where It Should Be Used

Curved tempered glass can be used in a monolith or set in *laminated glass* or *double glazing*, ensuring the performance of each of the properties of this type of glass.

Whether its *double glazing* or *laminated glass*, both of them or other monoliths must have the same curvature.

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[2] A spontaneous catastrophic fracture, often referred to in *tempered glass*, is rare. Some of the causes of this fracture can include the presence of impurities such as nickel sulphate crystals, incomplete tempering, forces on the glass frame, accumulation of surface risks (microcracks) or excessive exposure to the sun.

8.8.6 Fire-Retarding Glass

The first *fire-retarding glass* was *wired glass*, which was first retailed in 1895. *Wired glass* remains in place after breaking so it was chosen at the time to prevent the spread of fire and smoke inside and between buildings. Even nowadays *wired glass* has retained an important share of the market for *fireproof glass*.

8.8.7 Double Glazing

Double glazing uses two (or more) panes of glass, separated by a spacer bar that seals the cavity width (usually filled with dehydrated air) between the two glass panes. The glass–air–glass system is hermetically sealed by a frame especially designed for this purpose. In addition to the frame, the presence of a desiccant is recommended to absorb humidity inside the glass and ensure good performance long term.

Glass that is simply *annealed* or *tempered glass*, *transparent* or *coloured glass*, *silkscreen printed glass* or *tempered glass*, as well as *low-emission glass*, *anti-reflection glass* or *self-cleaning glass*, can be used in *double glazing*. The thickness of the glass used can vary, as well as the thickness of the air cavity between the glasses.

Double glazing improves thermal performance, keeping the inside of the buildings more comfortable and reducing running costs. The thermal barrier that the air cavity creates between the two panes of glass means that the inner sheet of glass does not cool down below the dew point, minimising condensation on the inner layer of glass, as well as other problems associated with humidity.

How It Is Produced

Double glazing is generally made by companies involved with the production of *float* glass. The glass used in *double glazing* is fitted in frames, in whose quality the performance of the *double glazing* will largely depend.

Where It Should Be Used

The combination of *low-emission* or *anti-reflection coatings*, *coloured glass*, *rolled plate glass* and *laminated glass* offers a range of configurations, able to respond to the most demanding of projects.

Double glazing is for outdoor use.

Colour

Glass that is *coloured* can be better integrated into the building to suit the surrounding architectural elements, as well as improving solar control. *Coloured glass* often requires a thermal treatment.

Argon

Using argon in the air cavity instead of dehydrated air (in the *double glazing*) increases the thermal performance.

Double Glazing with a Built-In Blind

By incorporating a built-in blind to the *double glazing*, the project has new possibilities.

Double glazing can be produced to suit the project requirements, in terms of the size or type of glass.

Specific Recommendations for Double Glazing

- Assembly

  Although insulation increases with the thickness of the air pocket in *double glazing* for the transfer of heat through conduction, for convection, the opposite is true. Insulation is optimised for air cavities that are 16 mm thick.

  Humidity has more heat potential than other forms of air, so drier air significantly reduces the flow of heat through the window. A desiccant (drying agent), molecular sieves or silica gel, can affect the long-term performance, as the desiccant absorbs humidity that may pass through the sealant.

  The quality of the frames is critical in *double glazing*. The stress caused by strong winds can be enough to misplace the outer glass and cause it to touch the inner glass, reducing or removing the air cavity. This situation can be avoided by pressurising the air cavity or fitting a spacer to prevent the two pieces of glass from moving.
- Compatibility

  The edges of the *double glazing* should be clean and free from defects. The frame surrounding the insulation should ensure that it is impermeable to prevent water from getting in between the glass. Pliable frames are recommended.
- Gurantee

  Double glazing generally has a 10-year guarantee, provided by the manufacturer, against low visibility caused by dust, humidity or films on the inner surface of the *double glazing* or by the lack of insulation at the edges, caused by a defect in the materials.

  The edges can crack due to vibrations or high temperature rises, and this leads to a crack in the *double glazing*.

Bibiliography

Glass History

Tait H (ed) (1999) Five thousand years of glass. British Museum, London

Mendes JA (2002) *História do Vidro e do Cristal em Portugal*, Colecção História da Arte, Lisboa, Edições Inapa

Redol P (2003) O Mosteiro da Batalha e o Vitral em Portugal nos séculos XV e XVI, Câmara Municipal da Batalha

Hummel RE (1998) Understanding materials science: history, properties, applications, 2nd edn. Springer, New York

Glass Structure and Properties

Navarro JMF (1991) El Vidrio, Consejo Superior de Investigaciones Científicas Fundación Centro Nacional del Vidrio, Madrid

Zarzycki J (1982) Les verres et l'etat vitreux. Masson, Paris

Doremus RH (1973) Glass science. Wiley, New York

Kingery WD, Bowen HK, Uhlmann DR (1976) Introduction to ceramics. Wiley, New York

Tilley R (2000) Colour and the optical properties of materials. Wiley, New York

White MA (1999) Properties of materials. Oxford University, Oxford

Forde M (ed) (2009) ICE manual of construction materials, vols I and II. ICE Manuals, Thomas Telford Limited

http://www.glassonweb.com

Glass Preservation and Maintenance

Brantley LR, Brantley RT (1996) Building materials technology. Structural performance & environmental impact. McGraw-Hill, Inc, New York

McLellan GW, Shand EB (1984) Glass engineering handbook. McGraw-Hill, New York

Ashurst J, Ashurst N, Faulkner P, Harrison H, Kerr J, King E (1999) Wood, glass and resins, practical building conservation, English Heritage Technical Handbook, vol 5. Gower Technical, Aldershot

Appleton J (2003) Reabilitação de Edifícios Antigos. Patologias e Tecnologias de Intervenção, Edições Orion

Navarro JMF (1991) El Vidrio, Consejo Superior de Investigaciones Científicas, Fundación Centro Nacional del Vidrio, Madrid

Glass Products and Manufactures

http://www.glassresource.com/sneakpeek/sample15.htm
http://www.glassindustry.info/
http://www.glasslinks.com/
http://www.saint-gobain.com/fr/html/index.asp
http://www.dupont.com/safetyglass/lgn/index.html
http://www.us.schott.com/tgd/english/products/okasolar2.html
http://www.AFG.com

http://www.sisecam.com/
http://www.glaverbel.com/
http://www.oldcastleglass.com
http://www.guardian.com/en/index1.html
http://www.saflex.com/pages/
http://www.glasshotline.com/jge/floatbath.htm
http://www.pilkington.com
http://www.owenscorning.com/

Glass recycling

http://www.escritadigital.pt/edicoes/apemeta/DesenvAssociados.asp?idutil=4659
http://www.minproint.com/

Glass Societies and Organizations

United glass corporation—usa
International Commission on Glass, ICG
http://www.ceramics.org/education/ccicourses.asp
http://www.glass.demon.co.uk/
http://www.glassindustry.info/list.php?gSearch=solar%20control%20glass
http://www.glasschange.com/assn/gl000248.html
http://www.britglass.co.uk/aboutbritglass/default.htm
http://www.solgel.com/articles/Sept01/teo.htm
http://www.shef.ac.uk/~icg/
http://www.ukic.org.uk/
http://www.glassindustry.info/index.php?category=168
http://www.win.tue.nl/macsi-net/WG/WG4.html
http://www.icemna.org/eresglss.htm
http://www.unido.org/en/doc/4722

Glass Technical Publications

Glass-Technology International
http://www.usglassmag.com
http://www.glassonline.com/PublicationsNew/worldglassdirectoryNew.htm

Glass Project Software

RUBIS©, DTU (Saint-Gobain)
SciGlass
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Ornamental Stones

9

Pedro Miguel Amaral, Jorge C. Fernandes, Vera Pires,
and Luis Guerra Rosa

Abstract

The present chapter introduces stone as a construction and building material. State-of-the-art information on aspects concerned with terminology from the stone sector, as well as a summary of the general production chains, are firstly presented. Afterwards, stone materials are presented according to several of the existing classes. Views on microstructural features and physical-mechanical differences between classes were also included. The subsequent section, more extensive, describes the physical-mechanical properties, test methods, test standards and main regulations for the several stone construction products. Harmonized standards for stone products and factory production control requirements according to CE marking requisites are described, followed by a detailed description of the test methods and the usual physical-mechanical behaviour of the main stone classes. Following, stone construction products and their requirements are introduced according to specific applications. A particular analysis of the fixing systems for stone cladding is made. The final part of this chapter is dedicated to conservation, durability and maintenance of stone construction products. A final approach to stone life cycle was also included. Therefore, the aim of the present chapter is mainly to describe the stone construction product requirements, suitability criteria and the methodologies inherent to the technology for applying natural stone products.

Keywords

Natural stone • Granite • Limestone • Marble • Suitability • Requirements • CE marking • Physical-mechanical characterization

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M.C. Gonçalves, F. Margarido (eds.), *Materials for Construction and Civil Engineering*, DOI 10.1007/978-3-319-08236-3_9

9.1 Introduction

Stone has been a constant material not only in historical but also in contemporaneous buildings. In fact, stone is applied for several uses since the beginning of mankind. Compared to other abundant natural material, such as timber, stone was preferably chosen for building shelters. Firstly, through natural caves and later evolving as building material for houses, temples, roads and tombs. In stone construction, walls were firstly built with stones as structural elements, with piers, columns and buttresses of the same material. Stone is not only one of the most abundant materials on earth, but it is also one of the hardest, secure, solid, most durable natural materials. Figure 9.1 depicts several examples of historical and contemporaneous stone applications.

As men learned to extend the architectural possibilities of stone construction over the centuries, increasingly sophisticated methods for joining stones developed and the design of building facades and pavements began to be considered separately from the construction of the load-bearing walls and floors.

Fig. 9.1 Examples of historical stone applications in floors and cladding: (**a**) floor of the surrounding area of Padrão dos Descobrimentos (Lisbon); (**b**) interior floor of the Milano "Duomo" in Italy. Examples of contemporaneous stone applications: (**c**) Museum Casa de Serralves (Oporto) Portugal; (**d**) black diamond building in Copenhagen, Denmark

Stone has always been a crucial part of the material culture of the human race. Mankind faced the need to process stone as early as the beginning of its development.

Today numerous systems and fixing configurations are available for installing stone. As will be presented further on this chapter, many factors must be considered by the designer/architect in both selecting and dimensioning stone and support systems to prevent premature failure and to ensure long-term durability.

EU countries are traditional users of natural stone and stone products and have the highest per capita consumption worldwide. In square metres, the top 10 EU consuming countries represent 84 % of the total global consumption of finished stone products in which stone for cladding is included.

Besides its general use there is not always a direct connection with knowledge between all the intervenient that choose, build and use the natural stone materials.

Stones in buildings (exterior) are subjected to several exposures such as mechanical loads due to wind pressure, earthquakes, vandalism, thermal loads due to sunshine, freezing or fire, and chemical effects due to salt, acid rain or polluted air. Some of these exposures, such as the mechanical loads caused by wind or the thermal loads due to freeze-thaw cycles, are easy to predict owing to the possibility of dimensioning calculus based on specific data according to the CEN Eurocodes 0, 1, 3, 8 and 9. Other exposures, like the effect of decay caused by heat, freezing, thermal shocks, salt and pollution, on physical-mechanical properties of stones, are not fully understood. Work can still be done on several fields of decay quantification that allow a most suitable and accurate selection and dimensioning of stone materials.

Improving dimensioning processes involves individually evaluating "uncertainties", which are variables that affect system's reliability. Reducing risk of failure increases system trustworthiness. The process of refining risk begins during initial stone selection and continues even after the building is finished, through maintenance inspections and repair. This allows identifying any variables that were not initially predicted and helps to improve stone service life.

The terms "rock" and "stone" are commonly used and occasionally might lead to confusion when someone starts to have interest in these matters. Rocks can be defined as an aggregate of one or several minerals joined to one another in a more or less tight structure, which determines the properties, such as colour, strength, porosity and durability. Rocks constitute one of the basic components of earth crust and are naturally occurring, inorganic, mainly crystalline solids that have definite physico-chemical properties.

When a rock is shaped and worked to satisfy man's needs, it becomes a "stone". Building stone, ornamental stone, decorative stone, sculptural stone and aggregate stone are all possible "products" after a rock is selected and cut to a certain dimension (with or without surface finish).

Ornamental stones are a particular, but very substantial, segment of the stone industry in general. The three main classes of rocks (sedimentary, metamorphic and igneous) can be commercially exploited into what is commonly defined to be the ornamental stone industry. Common stones are normally seen as low cost materials without any other application either than its use in the composition of concrete or to build the most traditional walls and floors (traditional pavements). On the other hand, ornamental stones are normally associated with wealth as they are always very expensive in almost all outward appearance. Within the main types of stone applied in the ornamental stone sector, marble and granite appear as the two "noblest" materials.

To better classify a rock or stone, there is the need to know and understand about their formation processes and their structure. The knowledge on building materials such as stone should not be limited to their physical-mechanical properties. Every project with stone should take into account its origin, quarrying method, availability, the existence of suitable production methods and maintenance. Generally it is advisable to have a comprehensive knowledge over stone as a whole because each stage of the process has an important role to play in the final application.

Figure 9.2 depicts a scheme of some of the key stages concerning a common stone production cycle in Portugal.

In a relevant project it is extremely important to have a previous knowledge on the selected stone production cycle. From this it will be possible to evaluate if a certain quarry is able to supply all the amount of necessary material. Also it will be possible to evaluate which quarrying methods are most suitable for each stone type, since some may clearly produce internal fractures on the blocks. Another issue of importance is to assess if the stone exists in other quarries in case any repair has to be done [1].

During production stage it is important to assess if the factory has all the available technology to accomplish not only tolerances but also homogeneity on the selection, gloss and the choice of the correct finishing treatments according to the project requirements [2, 3]. The knowledge on the stone production stages and of its limits may help to reduce misunderstanding during the work and also decrease costs for the project (with less rejected material).

Material selection is another crucial stage that should be discussed on the project level [4]. It should not be expected that a particular marble type has the exact same hue when cut into slabs. Differences should be expected when selecting stone materials. It is also important for the engineer to have knowledge concerning the selection criteria of each stone supplier so he could better deal during negotiation and selection stages.

However all the abovementioned questions may be evaluated in a separate way, there is one question that should be common to all of them: environmental concerns [5].

Uncontrolled quarrying without a proper territorial frame is one of the main negative aspects when dealing with natural stone products. However, in Europe a large effort is being done in the main stone players in order to regulate inadequate quarrying. Also the use of new stone quarrying technologies is on the way to avoid excessive waste and intents to optimise each quarrying area [6]. This topic will be further approached in the end of this chapter when discussing the life cycle assessment of stone products.

Fig. 9.2 Examples of a common stone production cycle in Portugal: (**a**) block quarrying, (**b**) block cutting into slabs, (**c**) slabs polishing, (**d**) slabs final cut for smaller slabs or tiles, (**e**) packing and dispatch

9.2 Stone Material Structure

The most generic descriptions for defining each type of stone state mainly its compounds and the corresponding space distribution [7]. Besides the definition of the crystalline structures shown in each group minerals that form the rock, there is a broader definition to describe not only the chemical and mineralogical composition of each petrous material but also its texture. The material's structure, like previously mentioned, is the most determinant factor for selecting any type of stone when being applied as a construction material. Although it seems complex, a good understanding of the main stone structural features allows not only having an idea of the macroscopic properties but also prevent the occurrence of certain phenomena that are not related with properties normally determined. This knowledge establishes the slim line between absolute success of an application and the failure that derives from an inadequate use of the material, often unfairly stated as a problem derived from the stone.

Nowadays, the observation of anomalies resulting from an inadequate material selection results in pathologies, which are many times difficult to evaluate. Usually, problems are avoided by simple preliminary analysis between materials and applications. It should be emphasised that knowledge and experience in using these materials allow, almost always, an adequate prevention.

Rocks are divided into three major groups: igneous, metamorphic and sedimentary [8]. The first group of rocks includes granite, basalt, syenite, gabbro and diorite. In the metamorphic rocks marble is the most known type. However, other metamorphic rocks are also used in the industry, such as quartzite and gneiss, along with other materials in expansion such as slate and schist. Last, the group of sedimentary rocks includes calcareous limestone, dolomite and among other less employed by the ornamental stone sector.

Despite what was previously stated, this sort of classification is not commonly used by industry. Ornamental stones are often classified according to commercial aspects. In general it is common to observe the division of granite, marble and limestone. In certain countries, the use of schist implicates the use of another particular type of stone with ornamental use, the slate [1].

The separation of rocks in these three major groups also represents the division between the "softer" and "harder" rocks, which is mainly associated with the technological processes used to process these materials, as well as the typical applications when we expect a given durability. In this sense, terms like "granite" and "marble" are used to designate silicate and carbonate rocks, respectively, employed or not with ornamental purposes, but able to be submitted to a surface finish.

9.2.1 Granite

Granite is an igneous rock resulting from deep primary and secondary magma consolidation (intrusive plutonic rocks) [4]. Macroscopically, they are hard stones and usually difficult to be mechanically processed. They show a wide variety of tonalities (white, grey, blue, pink or red) and a granular texture ranging from fine (bellow hundreds of microns) to coarse (up to a few tens of centimetres). As referred, from the commercial point of view the term granite includes other sorts of stones showing some common traces: (1) having similar chemical-mineralogical compositions; (2) being silicate rocks; (3) implicating a similar production process.

The structural description of these materials is primarily made through petrographic characterisation. The main attributes described by petrographic analysis are

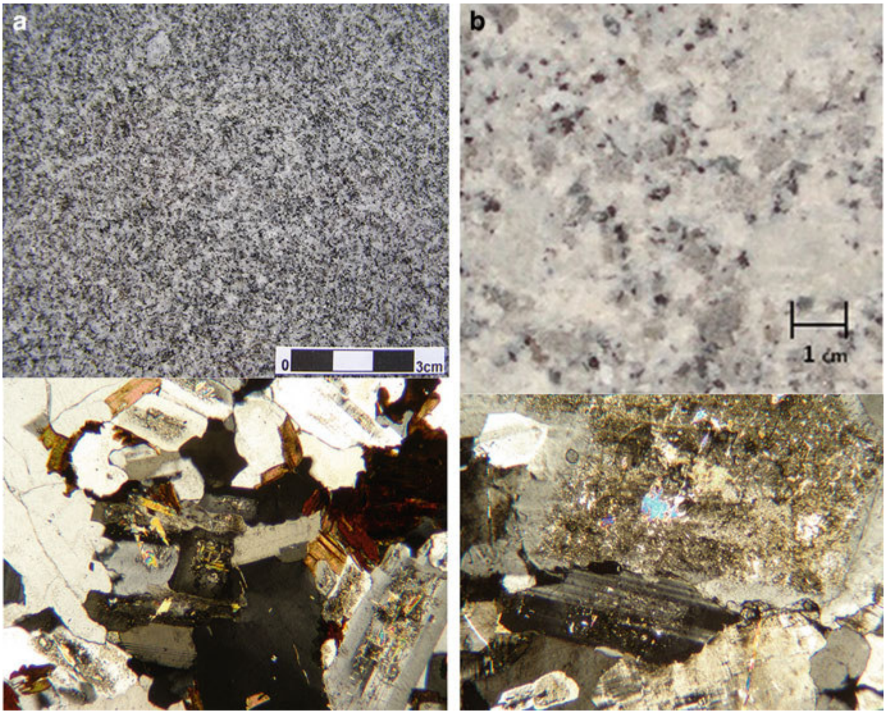

Fig. 9.3 Aspect of some granite materials quarried in Portugal. (**a**) Azul (Blue) Alpalhão (or SPI); (**b**) Cinzento (Prey) Pedras Salgadas; both macroscopic and microscopic textures

composition and texture. The classification of igneous rocks (usually used as ornamental) is made according to the simplified diagram of Streckeisen [1]. Generally, granites are described as plutonic rocks with holocrystalline texture, comprising essentially by feldspar (potassium and plagioclase) and quartz. Some accessory minerals are also visible in granites (less than 10 %wt), such as mica (biotite and muscovite). Figure 9.3 shows several aspects of Portuguese granite, where it is possible to compare the macro- and microscopic (petrography) texture.[1]

Another important classification of granite is made by determining its chemical composition. Typically granite is described by having a silica (SiO_2) content higher than 40 %wt (ultrabasic rocks). However, the common types of granite show more than 60 %wt in silica. Other common compounds of granite are alumina (Al_2O_3), iron oxide III (Fe_2O_3), magnesium oxide (MgO), sodium oxide (Na_2O) or potassium oxide (K_2O). The results from chemical analysis can originate an estimate of the mineralogical composition of rocks.

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[1] Although not so common, microstructural texture can be equally used by the term microstructure.

9.2.2 Marble

Marbles are metamorphic stones formed at a variable depth from the earth surface [7]. Marble forms from mineral and textural transformations (complete recrystallisation) from other rocks with different origins. Typically the main two types of metamorphism agents occurring to form marble are pressure and temperature. This event derives in a situation where these materials show higher variability in their properties when compared to granite. Despite from what is normally known from common sense, some marbles show similar properties (e.g. mechanical) compared to granite. Therefore, marble selection should be compliant with its origin, in particular its microstructure. For example, marbles showing light tonalities (or even white) are originated from pure calcareous rocks (sedimentary) which implicate sometimes similar properties compared with limestone. Marbles with different colours or veins, result from the presence of minerals formed from local impurities in the original calcareous bed.

Taking into account the two major rock commercial divisions (granite and marble), the limestone (a rock with strategic importance in some markets such as Portugal and Spain) will be included in this section. This rock has almost the same chemical and mineralogical composition of the majority of the marble (except those with a great number of minerals formed by impurities). Therefore, their structure should be analysed in the same line as that performed in marble.

In general the structural characterisation procedures of carbonate rocks are similar to granite. In particular, petrographic and chemical analyses are normally performed. Marbles from either show high level of calcite or dolomite (whereas calcite is subordinated or absent) along with a granoblastic texture, sometimes sacaroid, of medium to fine grains. Marbles explored in countries like Portugal rarely show coarse grains, but are often rich in colour pigmentation, causing large variations in tonality, even inside the same quarry. In the particular case of limestone, one of their main characteristics is exhibiting a high level of stratification, sometimes with a variable interlayer dimension. Discontinuity planes normally separate these layers with a structure often showing the detritic elements that reveal the origin of this rock.

In Fig. 9.4 it is possible to observe the aspect of various types of marble and limestone from Portugal and compare the macroscopic and microscopic texture (petrography).

9.2.3 Slate and Other Schists

Slates and schists are a particular circumstance of metamorphic rocks. Slates are known by their dark/bluish colour and by showing schistosity planes [1]. Slate structure usually implies an easy rupture on its schistosity planes. However when load is applied perpendicular to the schistosity planes its mechanical strength can be higher than most of the limestones. Also in this stone group, it is possible to find another stone named quartzite which has gained market in the last few years.

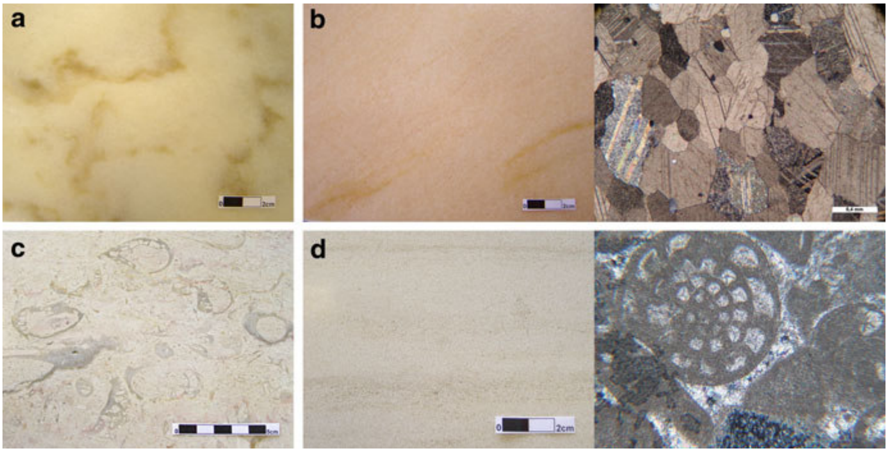

Fig. 9.4 Aspect of several types of marble and limestone rocks from Portugal. (**a**) Creme (cream) venado (veined), macroscopic texture; (**b**) Rosa (pink) aurora, macroscopic texture; (**c**) Lioz, macroscopic and microscopic texture; (**d**) Moca creme (cream), macroscopic and microscopic texture

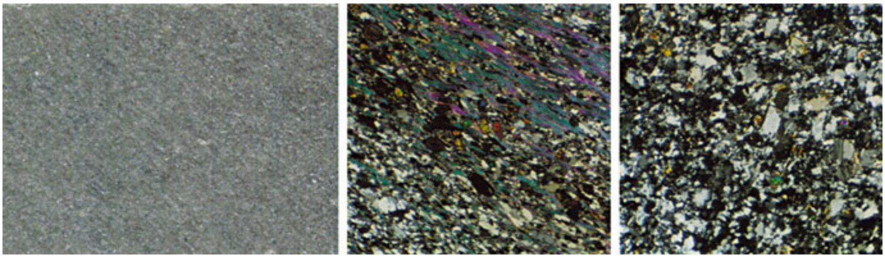

Fig. 9.5 Example of a schist stone: high quartzite from Norway macro- and microstructure

Its structure is more compact than most slates and several colours are available from light green to whitish hues.

When using, for example, for cladding a highly anisotropic material like slate, schist or quartzite, the orientation of the schistosity planes towards the anchor system requires special attention. A properly executed dimensional stone cladding should be designed and installed within the capabilities and limitations of the slate's support system to resist all active forces or actions (Fig. 9.5) [9].

Macroscopic, along with petrographic analysis, is considered the first characterisation step to the knowledge of stones structure.

Macroscopic analyses describe the main aspects of a stone type such as colour, veins and all the features that may describe a certain stone type. One of the first features when selecting stone is the aesthetic properties, mostly defined by colour. It is generally assumed that stone colour might change when exposed to external agents, but variations in colour can be seen as unpleasant.

Changes in colour might be the consequence of either staining by foreign materials or discoloration by a change in minerals structure. Stone colour stability is an essential parameter that should be understood and monitored [6, 10]. No standardised method for measuring colour has yet been established for ornamental stones. Such standardisation is particularly necessary for batch colour selection, particularly of stones constituted by minerals of very different colours or patterns, such as granites and marbles.

On a more detailed approach, petrographic analysis is considered as an essential examination tool not only for systematic and descriptive aspect analysis of rocks but also because it is intrinsically related with rock origin and rock natural history [8]. From petrographic analysis it is possible to acquire several data beyond the assignment of a petrographic name to the stone (these data might include aspects related with the original rock mass and local natural history).

Most of the rock-forming minerals appear translucent when examined in transmitted light. To allow this analysis, slices of rock, thin sections of approximately 0.03 mm thickness, have to be produced and mounted on glass. (At the end of the preparation, thin sections can be covered with glass or left uncovered but polished.)

Generally, a petrographic analysis performed by experienced technicians will provide information on rock minerals, minerals proportions and rock texture. If the fully mineral identification is not possible, complementary characterisation methods might be used (such as X-ray diffraction).

Guidelines for petrographic description of the main rock types are referred in the European standard EN 12407:2007, which allows a more uniform characterisation procedure.

Petrographic analysis has other fields of application besides rock classification according to petrographic names. This analysis technique is also applied to study mineral features concerning durability (such as primary alterations reactions on fresh rock specimens) that might influence the final-product mechanical strength. In this dissertation, this was the main goal for petrographic analysis. Besides mineral identification and texture definition, rock thin-section analysis allows highlighting of features concerning common primary alteration reactions for certain minerals.

9.3 Physical-Mechanical Properties: Specifications, Standards and Regulation

The European internal market offers to the stone producers the possibility of enlarging their market, but it is also a cause of new obligations. This is due to the fact that the technical barriers to trade can be only removed if a harmonisation of different regulations and specifications in force within different European countries is reached. It is therefore essential for the stone producers to know the rules set up by the European Community to reach harmonisation.

The first attempt of the European Community to remove technical barriers to trade was to include detailed technical specifications in directives, but it didn't work so that in 1985 a "new approach" to this problem was decided: directives should state the obligatory essential requirements, while the technical specifications to implement the directives should be entrusted to voluntary standards organisations.

In 1961 the national standards bodies of some European countries set up the European Committee for Standardization (CEN).

This is why the European Community decided that CEN was the organisation competent to develop European harmonised standards or to identify existing standards which will offer technical solutions to meet the essential requirements of the directives.

Through the years, CEN has grown: now the national members constituting CEN are 22 European countries (Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Hungary, Iceland, Ireland, Italy, Luxembourg, Malta, the Netherlands, Norway, Portugal, Slovakia, Spain, Sweden, Switzerland and the UK). They provide the secretariats of CEN Technical Committees. The members develop and vote for the ratification of European Standards.

In the construction sector, the reference regulation is the Construction Products Regulation (EU) № 305/2011 of the European Parliament and of the Council of 9 March 2011 laying down harmonised conditions for the marketing of construction products and repealing Council Directive 89/106/EEC (CPR).

According to this regulation, construction products may be placed on the market only if they are suitable for a given intended use. That is to say if they have such characteristics that the works in which they are to be incorporated, assembled, applied or installed, can, if properly designed and built, satisfy the following essential requirements:

- Mechanical resistance and stability
- Safety in case of fire
- Hygiene, health and the environment
- Safety in use
- Protection against noise
- Energy economy and heat retention

According to the CPR all construction products suitable for a given intended use must bear the CE mark and be accompanied by an attestation of conformity. The declaration of performance must be based on the results of initial type testing of the product and on factory production control (FPC). There are two different possibilities for the declaration of performance for the stone construction products, which differ in the way these tasks are carried out:

- Initial type testing of the product by an approved laboratory and FPC carried out by the manufacturer (System 3)
- Initial type testing and FPC carried out by the manufacturer (System 4)

The characteristics to be controlled on construction products are given in the mandates issued by the European Commission to CEN for the drafting of harmonised standards [11–13].

9.3.1 CE Marking for Natural Stone Products

The CE marking of construction products is understood as the most significant change being faced by the construction industry for a decade. Understandably, wholesalers are looking to their suppliers to provide them with the information and test results that they will need in order to be able to CE mark their work.

The introduction of CE marking on building products is taking place as part of the continuing efforts of Europe to harmonise standards so that the products of all the countries of the Union can compete on a level playing field.

As suppliers of finished product, stone processors will be responsible for the accuracy of the information relating to the CE mark, even when it has been provided by the company that supplied the stone.

The major stone quarry companies in Europe have already carried out the necessary testing for CE marking on their stones or are in the process of doing so. Those that supply products such as paving, flooring or cladding that will have to be CE marked have either already marked it or will shortly be doing so.

If stone slabs are used for wall lining, flooring or steps, the stone company that cuts the slab for that purpose will have to issue a CE mark. CE marking is also compulsory on tiles, paving, cladding and roofing.

For stone products, there is no pass or fail, as such, but a requirement for test information to be supplied to show the stone is consistent with a declaration of performance from the manufacturer. The responsibility for the CE mark information being correct transfers to the stone company when it sells its products, even though the information has originated from the stone supplier.

The responsibility for CE marks transfers to wholesalers when there is a supply chain—for example, in the distribution of tiles or paving. It is the responsibility of a distributor to ensure the information is correct, even though it has come from the supplier, and to withhold a product from the market if they believe it is not fit for purpose, even if it is CE marked and all the relevant test results are presented.

Making sure the products do meet the standards claimed for them might mean wholesalers have to carry out sample testing to satisfy themselves that the information they have been provided is correct (Table 9.1) [14, 15].

Initial type testing shall be carried out at the first application of the corresponding standard or when a new product type is developed and whenever a significant change occurs in the raw material or the production process.

On the basis of the results of initial type testing for the determination of the essential characteristics, the manufacturer shall prepare the declaration of performance which authorises the affixing of the CE marking. The latter will be affixed only on finished products, but initial type testing can also be performed on samples taken from the raw material used to manufacture the product. The slip resistance, for example, being a function of the surface finish, must be determined on finished products [16, 17].

The CE marking shall be accompanied by general information (name of the manufacturer, last two digits of the year in which the mark was affixed, intended use and description of the product, reference to the relevant harmonised standard) and

Table 9.1 Harmonised standards for natural stone products [27]

Harmonised standards for natural stone external paving	
EN 1341	Slabs of natural stone for external paving. Requirements and test methods
EN 1342	Setts of natural stone for external paving. Requirements and test methods
EN 1343	Kerbs of natural stone for external paving. Requirements and test methods
EN 1469	Natural stone products—Slabs for cladding—Requirements
EN 12057	Natural stone products—Modular tiles—Requirements
EN 12058	Natural stone products—Slabs for floors and stairs—Requirements
EN 1467:2003	Natural stone products—Rough blocks—Requirements
EN 1468:2003	Natural stone products—Rough slabs—Requirements
EN 12059:2008	Natural stone products—Dimensional work—Requirements

Table 9.2 Thickness admissible tolerances for slabs for cladding

Nominal thickness (mm)	Tolerance
More than 12 up to and including 30	±10 %
More than 30 up to and including 80	±3 mm
More than 80	±5 mm

Table 9.3 Length and width admissible tolerances for slabs for cladding[a]

Nominal length and width (mm)	<600	≥ 600
As sawn with thickness ≤ 50 mm	±1 mm	±1.5 mm
As sawn with thickness >50 mm	±2 mm	±3 mm

[a] Deviation from flatness (except natural cleft/riven faces) should not exceed 0.2 % of slabs length and should not be larger than 3 mm

by the declared values of the essential characteristics. The label with the CE marking shall appear on any packaging and/or accompanying commercial documentation.

Additionally to the initial testing, the manufacturer shall exercise a permanent FPC and keep record of the results at least until the next control. FPC system shall be established and documented. The FPC system shall consist of procedures for the internal control of production. The results of the tests carried out during FPC shall demonstrate that products placed on the market conform to this document and with the manufacturer's declared values or classes.

The internal control shall consist of regular inspection checks and tests and the utilisation of the results to control incoming materials, equipment, the production process and the finished product.

Regarding products final measures, all measurements shall be carried out in accordance with EN 13373 and all measured values of individual units shall fall within the required tolerances (see examples in Tables 9.2 and 9.3 and Fig. 9.6).

Visual appearance shall always also have to be declared. The colour, veining, texture, etc. of the stone shall be identified visually, typically by a reference sample of the same stone suitable for providing a general description of visual appearance. The reference sample shall be provided by the supplier.

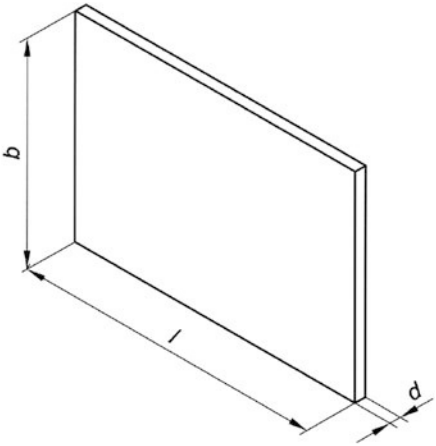

Fig. 9.6 Scheme showing slab for cladding generic dimensions according to EN 1469

A reference sample shall be an adequate number of pieces of natural stone of sufficient size to indicate the general appearance of the finished work. The dimensions of individual pieces shall be at least 0, 01 square metres (typical values are between 0, 01 and 0, 25 square metres in face area but may be more) and shall indicate the range of appearance regarding the colouring, the vein pattern, the physical structure and the surface finish. In particular the reference sample shall show specific characteristics of the stone, such as holes for travertine, worm holes for marble, glass seams, spots and crystalline veins (see Fig. 9.7).

The reference sample does not imply strict uniformity between the sample itself and the actual supply; natural variations may always occur.

If the processing of the stone involves the use of patching, fillers or other similar products for natural holes, faults or cracks, then the reference sample shall similarly display the impact of the same on the finished surface.

All the characteristics as shown by the reference sample shall be considered typical of the stone and not as flaws; therefore, they shall not become a reason for rejection, unless their concentration becomes excessive and the typical character of the stone is lost.

For products that are not under CE marking requirements and which do not have a harmonised standard, it is possible to suggest a technical specification that may help producers to know their products' physical-mechanical characteristics. Table 9.4 shows some examples of special products and their recommended characteristics.

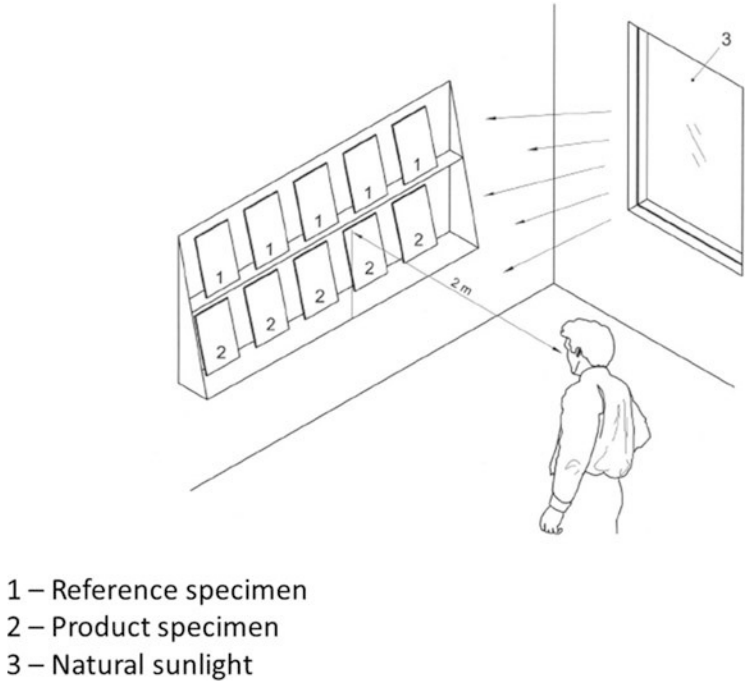

Fig. 9.7 Reference samples scheme example

Table 9.4 Examples of suitable physical-mechanical characteristics for special products

Product	Test
Funerary art	Flexural strength, frost resistance
Simple applications (sinks and basins)	Flexural strength, water absorption at atmospheric pressure
Technical applications (fire places)	Flexural strength, thermal expansion coefficient, water absorption at atmospheric pressure
Rough products (slabs and blocks)	Flexural strength, compression, apparent density, water absorption at atmospheric pressure, frost resistance, petrographic description
Note: for these products there exists a harmonised standard which is not mandatory but may be used as a reference	

Other standardised test methods for stone construction products are presented afterwards in Table 9.5.

Table 9.5 Natural stone test methods standards

EN 12670:2001	Natural stone—Terminology
EN 1925:1999	Natural stone test methods—Determination of water absorption coefficient by capillarity
EN 13364:2001	Natural stone test methods—Determination of the breaking load at dowel hole
EN 14581:2004	Natural stone test methods—Determination of linear thermal expansion coefficient
EN 14579:2004	Natural stone test methods—Determination of sound speed propagation
EN 14157:2004	Natural stone test methods—Determination of the abrasion resistance
EN 14205:2003	Natural stone test methods—Determination of Knoop hardness
EN 14066:2003	Natural stone test methods—Determination of resistance to ageing by thermal shock
EN 14231:2003	Natural stone test methods—Determination of the slip resistance by means of the pendulum tester
EN 14580:2005	Natural stone test methods—Determination of static elastic modulus
EN 14158:2004	Natural stone test methods—Determination of rupture energy
EN 13373:2003	Natural stone test methods—Determination of geometric characteristics on units
EN 14147:2003	Natural stone test methods—Determination of resistance to ageing by salt mist
EN 13919:2002	Natural stone test methods—Determination of resistance to ageing by SO_2 action in the presence of humidity
EN 12370:1999	Natural stone test methods—Determination of resistance to salt crystallisation
EN 14146:2004	Natural stone test methods—Determination of the dynamic modulus of elasticity (by measuring the fundamental resonance frequency)
EN 1926:2006	Natural stone test methods—Determination of uniaxial compressive strength
EN 1936:2006	Natural stone test methods—Determination of real density and apparent density, and of total and open porosity
EN 12372:2006	Natural stone test methods—Determination of flexural strength under concentrated load
EN 12407:2007	Natural stone test methods—Petrographic examination
EN 12440:2008	Natural stone—Denomination criteria
EN 12371:2010	Natural stone test methods—Determination of frost resistance
EN 13161:2008	Natural stone test methods—Determination of flexural strength under constant moment
EN 13755:2008	Natural stone test methods—Determination of water absorption at atmospheric pressure

9.3.2 Natural Stone Products Guarantee: Technical Certification

Stone has been a constant material not only in historical but also in contemporaneous buildings. In fact, stone is applied for several uses since the beginning of mankind. Compared to other abundant natural material, such as timber, stone was preferably chosen for building shelters. Firstly, through natural caves and later evolving as building material for houses, temples, roads and tombs. In stone construction, walls were firstly built with stones as structural elements, with piers, columns and buttresses of the same material. Stone is not only one of the most abundant materials on earth, but it is also one of the hardest, secure, solid, most durable natural materials.

StonePT certification brand (http://stone-pt.com/en/) is the result of a partnership between Assimagra—*Associação Portuguesa dos Industriais de Mármores, Granitos e Ramos Afins* and IST—*Instituto Superior Técnico*, with the aim of demonstrating the conformity of Portuguese natural stone products with the requirements established in technical specification. StonePT is part of the Collective Efficiency Strategy of Natural Stone Cluster, including the Anchor Project: Valuation of Natural Stone, approved under the COMPETE/SIAC. The main mission of this organisation is promoting and showing the credibility of its marks, in both national and international levels, as well as all the companies associated to it.

StonePT values are based on independence, technical assurance and credibility as a means to ensure its impartiality and integrity when in contact with different relating entities, assuring the adequate management of conflicts of interest [18].

StonePT technical specification intends to fulfil an existent void in natural stone market in what concerns the guarantee of origin and quality assurance associated to the transformation processes and, not less important, to the adequacy of use that each type of stone has for different applications, particularly those employed in construction.

Pilot companies certified with StonePT demonstrate to accomplish the requirements based on the following scope: product quality, service quality, time of delivery, complaint management, guarantee of origin and knowledge concerning suitability of use for each type of stone in each application (requirements for the end user).

StonePT brand aims not only to guarantee that stone products were produced with Portuguese stones but also that these products accomplish a pre-established range of physical-mechanical requirements established according to the technical specification. Stone products physical-mechanical requirements were established based on Portuguese stones wide characterisation work that has been made in last 20 years by several entities such as LNEG (Laboratório Nacional de Energia e Geologia), IST, Assimagra and FrontWave, Materials Engineering S.A [19].

Each stone company which applies for StonePT certification defines its products' scope. StonePT brand is valid not only for CE marking products with product harmonised standards such as:

- EN 771-6, Specification for masonry units—Part 6: Natural stone masonry units
- EN 1341, Slabs of natural stone for external paving—Requirements and test methods
- EN 1342, Setts of natural stone for external paving—Requirements and test methods
- EN 1343, Kerbs of natural stone for external paving—Requirements and test methods
- EN 1469, Natural stone products—Slabs for cladding—Requirements
- EN 12057, Natural stone products—Modular tiles—Requirements
- EN 12058, Natural stone products—Slabs for floors and stairs—Requirements
- EN 12059, Natural stone products. Dimensional stone work. Requirements

but also to other non-standard products such as fire places, balconies, slabs or blocks.

StonePT certification vision includes its recognition in the international market, so that Portuguese stone gains an already earned highlight and observed as a known add-value product.

It should be emphasised that StonePT brand should be seen as a product certification that not only demonstrates the commitment to the requirements but also allows the use of its mark in the frame of the image and communication strategy of the company.

The main features defined in the technical specification developed in this project were based on existing guidance documents used to evaluate and control the performance specifications of stone products and solutions such as rainscreen cladding solutions, mainly employed in the UK (Centre for Window and Cladding Technology (CWCT)) and the USA (National Building Specification (NBS) and American Society for Testing Materials (ASTM)).

More than the knowledge acquired from stone testing, StonePT specification aims to increase product suitability. Like this it will be easier to advise which stone better suits each product and which are the preferable settling methods and maintenance procedures.

The overall technical specification developed for the StonePT brand follows the main headlines:

1. Guarantee of origin—Only Portuguese stones with proved guarantee of origin are eligible.
2. Company management generalities—Comprises items regarding documents and records control, management responsibility and resources requirements.
3. Complaint management procedures and control of non-conforming product.
4. CE marking—Includes initial type testing and FPC items.
5. Stone products physical-mechanical suitability criteria according to the application requirements.

Fig. 9.8 StonePT® certified marks and sub-marks

6. Stone material traceability—Covers methods (based on codes, references, labels or others) which should allow to follow stone material from quarry to the final product.
7. Management review.

StonePT certified mark (see Fig. 9.8) is given to the companies which demonstrate accomplishment of the technical specification requirements presented above. StonePT technical specification has also been reinforced with three voluntary "sub-marks" related to the management, qualification and environmental respect, employed in those companies willing to demonstrate their social responsibility related to these fields.

Today, numerous systems and fixing configurations are available for installing stone on the exterior of buildings. As will be presented further on this chapter, many factors must be considered by the designer/architect in both selecting and dimensioning stone and support systems to prevent premature failure and to ensure long-term durability.

Stone projects generally start with the client or architect vision or inspiration. The drawings then tend to go to a project engineering section and progress until the final documents with an associate budget. Usually, none of these sections have considerably knowledge about stones performance according to the selected stone materials, type of application, environment or other issues which may affect stone performance. Most of the stones sold for cladding applications are prescribed assuming that they will not be settled in a chemical/physical demanding situation. However, once stone slabs are placed in different environments they become susceptible to a huge variety of stresses.

On the whole, construction products durability can be defined as their ability to resist wear and decay and continue to fulfil its function after an extended period of time and usage [10]. Stone product suitability will depend on how stone will respond to a new environment, different from the one where the rock was formed. New product reactions such as efflorescence or a change in colour are examples of possible stone reactions to regain balance when placed in new environmental conditions.

It is reasonable to admit that the possible available range of natural stones is huge and covers almost a complete colour spectrum varying in physical-mechanical properties, minerals and textures (even in the same stone type). Nonetheless, as this work describes, technical specifications for a particular application help in increasing stone products performance.

StonePT technical specification procedure follows the description from Fig. 9.9.

Fig. 9.9 StonePT technical specification scheme

9.3.3 Methods for Physical Properties Evaluation

Stone physical characterisation and evaluation can be made through the determination of several properties such as porosity, density, water vapour permeability, water absorption and colour.

Physical properties are often used as performance indexes for possible mechanical strength decay or alterations. The movement of water through stone “labyrinth” pore system is considered as very useful for predicting stone behaviour, as open porosity and the pore system are the main factors controlling water uptake and its transport inside the stone.

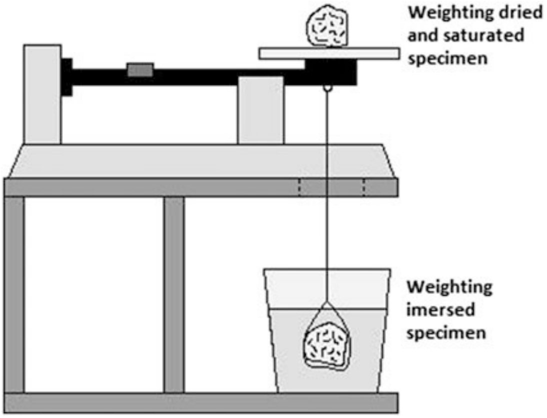

Fig. 9.10 Schematic representation of the test set-up necessary for apparent density and open porosity measurements

In this subsection, stone physical characterisation is above all focused on physical properties that might help to foresee the performance evolution of stone construction products under several exposures. Knowledge of stones' physical properties will help not only to understand the microstructure as it will complement the mechanical behaviour study clarifying several differences between the different stone types.

Water absorption at atmospheric pressure and water absorption by capillarity should be determined for a proper materials selection (despite the fact that this last method should only be applied when the stone specimens have an open porosity larger than 1 or 2 %).

Water plays an important part on building deterioration. As a consequence, it's extremely important the property determination that involves water transport throughout the stone pores (water absorption at atmospheric pressure and water absorption by capillarity). The water effects can be bad not only on stone construction products but also on concrete where the water can be conducted if a high porous stone has been applied. This situation is particularly dangerous when the stone is used in cladding. If, for example, the stone (tiles with reduced thickness) is fixed on the concrete only with cement and this started to corrode by the water that reaches the concrete through the stone pores, probably the tile will collapse and fall due to a lack of fixing.

The determination of water absorption at atmospheric pressure is made according to the standard EN 13755 and the water percentage can be estimated knowing the dry mass and the water saturated mass of the specimen.

Stones' apparent density is the quotient between the mass of the dry specimen and its apparent volume (limited volume by the external surface of the specimen, including the vacant). The open porosity (or apparent) is the quotient, in percentage, between the open pore volume and the apparent volume of the specimen.

Test procedure is described on the standard EN 1936 and establishes that apparent density and open porosity should be determined in vacuum (Fig. 9.10).

9.3.4 Methods for Mechanical Properties Evaluation

Mechanical properties of natural stone materials govern their limitations for structural applications where the material is usually required to bear a certain load or deformation. However, it is important to understand that mechanical properties can also be critical in non-structural applications (cladding/exterior facades), e.g. determining the lifetime of a component concerning the environmental aspects.

Mechanical behaviour assessment can also be very important for the evaluation on the way a particular material is processed, as failure is often initiated at microstructural imperfections. A useful philosophy in improving the strength of natural stone materials is to identify the nature of the failure origins of the material. The manufacturing process is then adjusted to eliminate the particular source of failure. In the natural stone materials context, one cannot change the formation process, but we can choose the "most suitable" combination of physical-mechanical properties which maximise their performance.

When defining stone construction materials' mechanical behaviour, it is clear that one of the most important properties is described by strength. For stone slabs for cladding and paving, strength is normally determined through laboratorial destructive flexural, anchorage or compressive tests, (EN 12372, 2006), (EN 13161, 2008), (C 1354-96, 2004), (EN 1926, 2006). These tests are used to evaluate stone mechanical quality and estimate the maximum allowable load before failure (Fig. 9.11).

The basic concern in cladding design to avoid structural collapse is established on the evaluation of the safety factor of the existing structures. The stress that leads to failure is intrinsically linked with the strength of the material. As a brittle material applied in building facades, stone faces a tensile and flexural challenge and therefore, it is extremely important to study stone materials strength regarding these requirements.

Usually included in the mechanical properties are some tests focused on the evaluation of some technological characteristics such as abrasion resistance and slip resistance (Fig. 9.12).

9.3.5 Methods for Durability Evaluation

Durability can be defined as the material ability to resist wear and decay and continue to fulfil its function after an extended period of time and usage. It is recognised, from the general knowledge, that all stones change with time and a relatively high number of works have been reported regarding the study of stone facades' durability due to decay effects.

A specific stone (and subsequent mineral) chemical, physical or mechanical change can be understood as the result reaction to new imposed natural or human conditions. Stone suitability will depend on how stone will respond to a new environment, different from the one where the rock was formed. New product

Fig. 9.11 Common mechanical test: (**a**) uniaxial compression strength test in cylindrical specimens; (**b**) flexural strength under constant moment; (**c**) dynamic elastic modulus; (**d**) fracture toughness; (**e**) microhardness test

reactions such as efflorescence and a change in colour are examples of possible stone reactions to regain balance when placed in new environmental conditions.

Stone durability changes depend usually on more causes than just mineralogy (stone alterability). Climate, environmental and human factors or facade

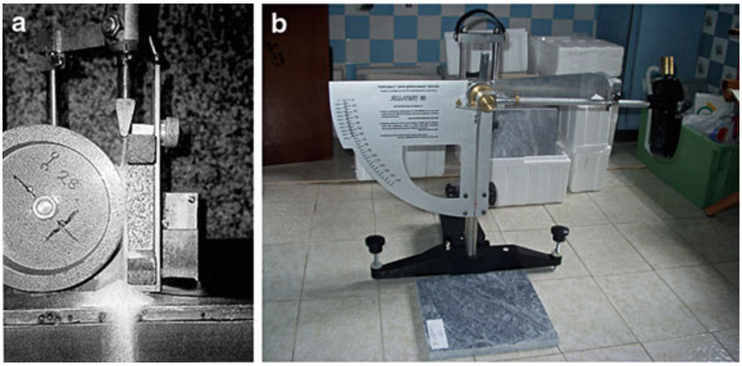

Fig. 9.12 Mechanical tests with technological focused: (**a**) abrasion resistance trough Capon method [1]; (**b**) slip resistance

Fig. 9.13 Salt fog chamber

architectural issues are just examples of aspects that might influence stone durability. Several times in practical applications, many agents such as temperature, moisture, pollution or salt might be present which makes the results interpretation harder.

Since European harmonised standards were developed for construction products, stone construction products' recommended testing procedures and requirements can be found in their own harmonised standard. A series of durability tests are recommended in this standard such as freeze thaw (EN 12371) [20] and thermal shock (EN 14066), besides the usual physical (density, porosity, water vapour permeability, water absorption at atmospheric pressure) and mechanical tests previously presented.

Other durability European standardised test methods exist such as (EN 14147) to test stone resistance to ageing by salt test or (EN 13919) to test stone resistance to ageing by SO_x; but they are not mandatory unless the buyer demands. Figure 9.13 depicts an example of a test chamber for salt fog evaluation.

9.3.6 Representative Physical-Mechanical Properties

It is reasonable to admit that the possible available range of natural stones is huge and covers almost a complete colour spectrum varying in physical-mechanical properties, minerals and textures (even in the same stone type). However, technical information with recommended values for a particular application is many times disconnected with particular environmental conditions. Meaning that several times stones may meet these values or comfortably exceed them and still damaging process may occur.

As a reference for stone cladding applications, for example, technical specifications and details concerning stones dimensions and physical-mechanical recommended values may be found in relative few works considering the relative high amount of stone settled in building facades. Examples can be found in the British Standard Code of Practice for Design and Installation of Natural Stone Cladding and Lining (BS 8298, 1989), in the Indiana Limestone Handbook, or in the Cahier du CSTB 3266.

Table 9.6 summarises the main physical-mechanical properties for a group of Portuguese granites, marbles and limestones. These values may be suitable in a first

Table 9.6 Examples of physical-mechanical properties for several Portuguese stones (mean values) and comparison with the mean values for each stone family (granite, marble, limestone)

Stone type	*Cinzento Alpalhão*	*Forte Rosa*	Granites	*Creme Venado*	*Rosa Aurora*	Marbles	*Moca Creme*	*Lioz*	Limestones
Compressive strength [MPa]	255	215	70-280	100	90	50-180	90	105	20-200
Flexural strength [MPa]	17	19	11-24	17	12	9-18	13	15	3-15
Elastic modulus [GPa]	50	59	40-70	73	62	50-100	45	58	20-70
Water absorption at atmospheric pressure [%]	0.29	0.20	0.10-0.50	0.05	0.06	0.10-0.50	2.34	0.11	até 13.00
Apparent density [g/cm^3]	2.66	2.64	2.60-2.70	2.71	2.72	2.60-2.90	2.52	2.70	2.00-2.90
Open porosity [%]	0.78	0.55	0-4 [4]	0.15	0.16	0.3-1.1	5.90	0.31	até 15
Thermal expansion coefficient [10^{-6} / ºC^{-1}]	8.8	9.8	7.0-14.0	11.1	7.3	7.0-12.0	5.3	3.3	3.0-5.0
Abrasion ressitance[mm]	4.0	0.3	-	2.6	3.7	-	4.0	2.2	-
Shock resistance – minimum fall distance [cm]	50	80-85	-	90	70	-	50	60	-
Durability [nº of freeze-thaw cycles without visual aspect changes]	25	25	-	25	25	-	25	25	-
Compression strength after 48 freeze-thaw cycles [MPa]	240	205	-	85	95	-	85	140	-

approach to compare and select different stone types. However, before each application the correspondingly recommended group of tests should be done according to the abovementioned test methods.

9.4 Stone Products and Application

Stone construction products can be grouped according to one of the three following categories [4]:

- Slab products
- Rough products
- Special products

This classification is intrinsically related with the application and final use of the stone product. Standardised products under CE marking can be included in the first category. Rough blocks and slabs can be included in the second group. In the third group it is possible to include all the special products that are customised according to each client requirements such as sinks, basins, fireplaces and others.

As it is possible to understand, each product category will have different requirements regarding the final application. Because of these differences, one of the technical comities for the stone sector (CEN TC 246) defined several products and the correspondingly test methods for CE marking testing [13].

9.4.1 Exterior Pavements (Tiles, Slabs, Setts and Kerbs for Floors and Stairs)

Product characterisation is fundamental since it is one of the most important factors for products' final quality:

- Slabs of natural stone for external paving (EN 1341): Any unit of natural stone used as a paving material, in which the working width exceeds 150 mm and also generally exceeds two times the thickness.
- Setts of natural stone for external paving (EN 1342): Small natural stone paving block with work dimensions between 50 mm and 300 mm and no plan dimension generally exceeding twice the thickness. The minimum nominal thickness is 50 mm.
- Kerbs of natural stone for external paving (EN 1343): Unit greater than 300 mm in length, commonly used as edging to a road or footpath.
- Modular tiles (EN 12057): Flat piece of natural stone square or rectangular in standard sizes, normally $\leq$610 mm obtained by cutting or splitting at a nominal thickness $\leq$12 mm.

Figure 9.14 shows several examples of the abovementioned products.

Fig. 9.14 Stone products with harmonised standards: (**a**) modular tile; (**b**) setts

9.4.2 Walls (Exterior and Interior)

As men learned to extend the architectural possibilities of stone construction over the centuries, increasingly sophisticated methods for joining stones developed and the design of building facades began to be considered separately from the construction of the load-bearing walls.

Today, numerous systems and fixing configurations are available for installing stone on the exterior of buildings. As will be presented further on this chapter, many factors must be considered by the designer/architect in both selecting and dimensioning stone and support systems to prevent premature failure and to ensure long-term durability.

Slabs for cladding (EN 1469) can be described as slabs cut to size which forms a wall covering and ceiling finishes for outside or inside use, fixed to a structure either mechanically or by means of mortar or adhesives.

Figure 9.15 depicts some examples of slabs for cladding.

9.4.3 Interior Pavements (Floors and Stairs)

A slab for floors (EN 12058) is a piece of natural stone obtained by cutting or splitting at a nominal thickness >12 mm. It is put on to a structure by means of mortar, adhesives or other supporting elements.

9.4.4 Slate and Stone Products for Discontinuous Roofing and Cladding

Slate rocks (EN 12326-1) can be described as rocks which are easily split into thin sheets along a plane of cleavage resulting from a schistosity flux caused by very low or low grade metamorphism due to tectonic compression.

Fig. 9.15 Slabs for cladding examples: (**a**) interior wall; (**b**) exterior cladding

9.4.5 Special Products

Besides the products already mentioned, there are also other products that are usually made by request with a great variety of shapes and sizes such as doorsills, windowsills, tables, statues or columns. However these stone products do not have a harmonised standard; it is possible to recommend a technical specification for them, taking into account the following requirements:

- Stone products should have mechanical strength for the intended use.
- Stone materials porosity should be suitable for the intended use. Higher open porosity stone types are not recommended for applications were humidity plays an important role.
- Stone materials should present good chemical resistance to sulphates, chlorites and nitrates.

9.4.6 Stone Construction Products Requirements According to Specific Applications

Stone projects generally start with the client or architect vision or inspiration. The drawings then tend to go to a project engineering section and progress until the final documents with an associate budget. Usually, none of these sections have considerably knowledge about stones performance according to the selected stone

Fig. 9.16 Schist slabs used as traditional masonry in Portugal

materials, facade type, environment or other issues which may affect stone durability. Most of the stones applications are prescribed assuming that they will not be settled in a chemical/physical demanding situation. However, as it could be seen from the previous sections, once stone materials are placed in different environments they may become susceptible to a huge variety of stresses (Fig. 9.16).

The knowledge about each stone's physical-mechanical behaviour and each application method limitations are extremely important for the final success of each work with natural stone materials. In some situations a stone type may not be totally suitable for the application.

Figure 9.17 depicts some of the main application of stone construction products.

Figure 9.18 depicts examples of special applications.

Table 9.7 summarises the main tests necessary for stone products physical-mechanical characterisation. Test results by itself are not a product quality warranty. Tests results should be compared with technical specifications that will help to understand the minimum requirements for each particular application. Table 9.8 specifies technical requirements for granite main applications.

Fig. 9.17 (continued)

Fig. 9.17 Examples of stone products applications: (**a**) stairs, (**b**) exterior cladding, (**c**) modular tiles for exterior walls, (**d**) modular tiles for interior walls, (**e**) slabs for interior cladding, (**f**) slabs for interior cladding and floors, (**g**) slabs for interior cladding, (**h**) slabs for floors and interior walls, (**i**) modular tiles for interior floor, (**j**) wood and stone combination for slabs for interior walls, (**k**) kitchen countertop and modular tiles

Fig. 9.18 Examples of special products with natural stone: (**a**) table, (**b**) multi-element column, (**c**) statue, (**d**) funerary art, (**e**) table base, (**f**) lintel

Table 9.7 Mandatory, voluntary and important requirements for the correct characterisation of natural stone products

Test	Exterior pavements (slabs or tiles)	Setts	Kerbs	Cladding (interior and exterior)	Interior pavements (floors and stairs)	Masonry	Slate and stone products for discontinuous roofing and cladding	Columns	Window sills	Cantilever slabs	Statues
Petrographic description	Volunt	Volunt	Volunt	Yes	Yes	Volunt	Volunt	Impor	Impor	Impor	Impor
Uniaxial compressive strength	–	Yes	–	–	–	Yes	–	–	–	–	–
Flexural strength	Yes	–	Yes	Yes	Yes	Yes	Yes	–	Impor	Impor	–
Elastic modulus	–	–	–	–	Impor	Impor	Impor	Impor	Impor	Impor	Impor
Water absorption at atmospheric pressure	Volunt	Volunt	Volunt	Volunt also by capillarity	Volunt also by capillarity	Yes also by capillarity	Yes	Impor	Impor	Impor	Impor
Apparent density	Impor	–	Impor	Yes	Volunt	Impor	Impor	Impor	Impor	Impor	Impor
Open porosity	Impor	–	–	Yes	Volunt	Volunt	Impor	Impor	Impor	Impor	Impor
Thermal expansion coefficient	Impor	–	–	Impor	–	Impor	Impor	Impor	Impor	Impor	–
Abrasion resistance	Yes	Yes	Impor	–	Volunt	–	–	–	–	–	–
Slip resistance	Yes	Yes	Impor	–	Yes	–	–	–	–	–	–
Anchorage strength	Impor	–	–	Yes	Impor	–	–	–	–	–	–

(continued)

Table 9.7 (continued)

Test	Exterior pavements (slabs or tiles)	Setts	Kerbs	Cladding (interior and exterior)	Interior pavements (floors and stairs)	Masonry	Slate and stone products for discontinuous roofing and cladding	Columns	Window sills	Cantilever slabs	Statues
Shock resistance	Impor	–	–	Impor	Impor	–	Impor	–	–	Impor	–
Durability (according to the application)	Yes (ice)	Yes (ice)	Yes (ice)	Yes (ice and SO_2) for exteriors	Yes (ice and SO_2) for exteriors	Impor	Yes (ice and SO_2)	Impor	Impor	Impor	Impor

Captions
Yes—mandatory for CE marking
Volunt—voluntary for CE marking
Impor—important characteristics that should be consider in a technical specification

Table 9.8 Technical requirements for granite main applications [1]

	Rough products, such as masonry, urban furniture, setts for pavements, columns, kerbs, porticos and other ornamental products	*Slab products*, used for interior or exterior such as tiles or slabs for pavements or cladding
Uniaxial compressive strength	>100 MPa (for exteriors)	>80 MPa (for exteriors)
Flexural strength	>11 MPa	
Water absorption at atmospheric pressure	≤ 0.4 %	
Water absorption by capillarity	Exterior areas with low exposure: ≤ 190 g/m^{2}s$^{0.5}$	Exterior applications: ≤ 90 g/m^{2}s$^{0.5}$
	Exterior areas with high exposure: ≤ 90 g/m^{2}s$^{0.5}$	
Abrasion resistance	Very intense traffic ≤ 0.4 mm	
	Intense traffic ≤ 0.7 mm	
	Strong traffic ≤ 1.0 mm	
	others—no restrictions	
Impact-shock resistance	Private use excluding kitchens: min. 0.3 m	3 cm thick minimum:
	Collective use: min. 0.45 m	Private use excluding kitchens: min. 0.3 m
	Public use: min. 0.6 m	Collective use: min. 0.45 m
		Public use: min. 0.6 m
		Strong applications: min. 1.0 m
Durability	Minimum nr of cycles for interior applications: without restrictions	
	Minimum nr of cycles for exterior applications: 25	
	Criteria	
	Materials with high frost resistance:	
	⇒ Water absorption between 0 and 0.3 and compression strength loss until 10 %	
	Materials with frost resistance:	
	⇒ Water absorption between 0 and 0.5 and compression strength loss until 20 %	
	Materials without frost resistance:	
	⇒ Water absorption higher than 0.5 and compression strength loss higher than 20 %	

9.5 Stone Fixing Systems

9.5.1 Direct Fixing Systems

A substantial number of applications using dimensional stone cladding in facades and, although in smaller number, roofs are accomplished using direct anchorage as the preferential technique. Being a widely used and very well-known technique, this text only intends to perform an abbreviated description of the technology. Therefore, direct anchorage theme will be approached only in a summarised way. It is well known that the facades using direct anchorage (and in a large part of the other construction products normally applied in this industry) can be accomplished in two ways:

- By adhesives—when the adhesive is the anchorage element. This adhesive can be a mortar glue, incorporating or not a special resin, a "glue cement" or a two-component glue without cement (commonly denominated "mastic"), usually constituted by a reaction of two components.
- By sealing—when the anchorage element is a mortar made of hydraulic whitewash or white cement that usually transforms these materials less susceptive for originating stains in natural stone claddings.

The direct anchorage of stone is widely spread in the more developed countries. One of the solutions more often applied is the use of anchorage adhesion by using the glue cement. These adhesives can come as only a one-component product that uses a pre-defined amount of resin incorporated in a mixture of powders or as product of two components with a pre-defined resin but not incorporating any mixture of powders. On the other hand, the adhesives, materials without cement, have been lately used to perform the anchorage of stone slabs in the facades. These several adhesives are usually made of epoxy resin that has a hardening process obtained through the chemical reaction of their components. Despite of being very practical, there is some reluctance in using this type of stone anchorage for external walls, essentially due to its cost, being normally found in particular situations when properly justified.

A current procedure to minimise future problem, it is advised, anyway, that the direct stone anchorage to external walls may be applied using reinforcement systems with connection wires, many times designated by "hairpins anchorage" (Fig. 9.19).

With the exception of the test that allows the determination of the anchorage resistance and of the classification given for the adhesion products by the supplier according to the EN 12004 standard, the lack of recommendations and specific standardisation for stone anchorage in external walls (namely, the acceptance criteria) originates the use of less appropriate anchorage products and incorrect application methods and techniques. Nevertheless, some glue cements are produced using recommendations described by a French technical document, "Cahiers du CSTB". This document does not recommend the use of cementitious adhesives on

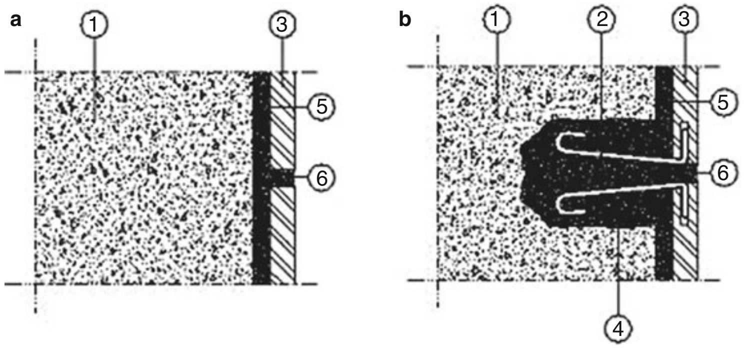

Fig. 9.19 Schematic representation of direct (**a**) and hairpin reinforcement (**b**) fixing systems for stone cladding. (*1*) Support (masonry or concrete), (*2*) hairpin reinforcement, (*3*) stone slab, (*4*) hairpin anchorage on the support structure, (*5*) fixing material (cement glue, epoxy resin, mortar), (*6*) spacing between the tiles

some natural stones as the schists and the slates due to their natural cleavage. The CSTB recommendation shows the general elements related to the product application on facades, in function of the rock porosity and the building height. The document refers that the superficial mass for the cladding elements must not cross 40 kg/m^2 [21, 22].

In relation to the use of these products, experience is usually the decisive factor in the final quality of the application. After preparing the support area correctly (leveling and cleaning) preparation of the support, the cementitious adhesive material application should be made using a double adhesion technique consisting application of the adhesives in both the support and in the back side of the stone slab. In case of glue cement, it should be dispersed on the support using a hand tool that has an appropriate tooth size, so that in the end we can observe a support with a continuous homogeneous layer with a regular thickness. The dimensional stone plates should be applied on the support by making pressure to guarantee the complete compression of the adhesive stripes left by the hand tool. This operation would be able to undertake that the slab backside is completely filled out with the adhesive and in contact with the support.

In direct anchorage, the cladding should foresee the use of spacing between the tiles with a minimum width of 4 mm. If the tile dimension increases, the spacing width must also increase. In large surfaces covered with slabs of natural stone, we should also foresee expansion joints. In case we observe the existence of structural joints along the walls, these should be respected, which implicates that these cementitious adhesives should not be used on this type of joints.

The most common pathologies found in facades are detachments and staining on the surface of the slabs/tiles. With the detachment the cladding panels could fall outward and in facades is particularly frightening, since it puts in risk human life's and goods.

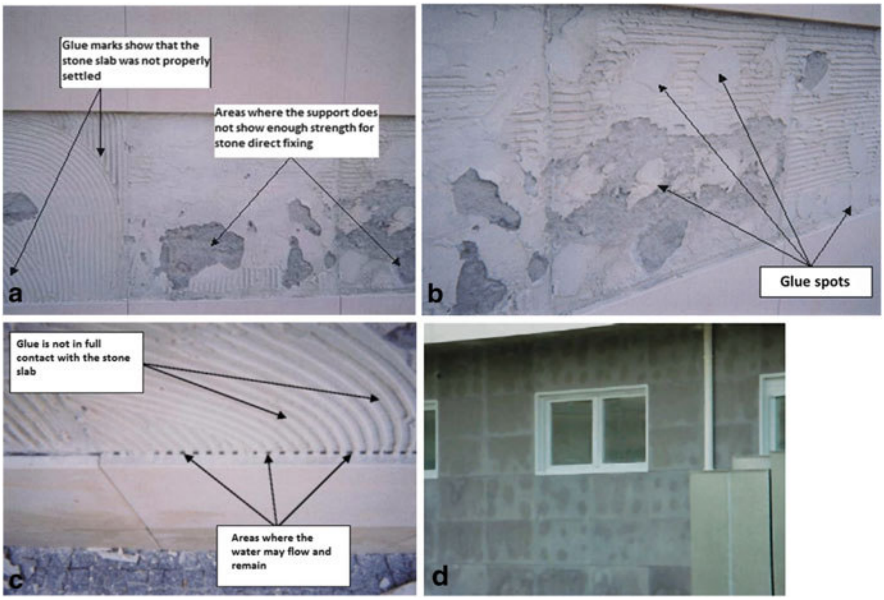

Fig. 9.20 Common pathologies presented by performing direct anchorage. (**a**), (**b**) and (**c**) after observing a detachment in the facades, the stone slabs were removed showing a deficient adhesion (identified in the subtitles); (**d**) limestone facade covering—where first we have observed water stains and later observed some saline efflorescence—in which the spacing joints were not filled out by project demands that have considered an aesthetic (effect of fixed facades by mechanical systems)

On the other hand, the stains that appear in the natural stone claddings have mainly an aesthetic damaging effect that affects the buildings facades. However, the resulting pathologies that are important to be detected are those that elapse from possible infiltrations in the buildings. Moreover, if there is any deposition of salts in the interface between the backside of the slabs and the adhesives, pressures will be generated due to the salt crystallisation, originating the detachment of the cladding. This "crystallisation pressure" present on the slabs surface originates a superficial degradation of the cladding materials. In Fig. 9.20 it is possible to observe a common pathology, normally found in buildings originated by several deficiencies.

It is important to refer that in spite of using some hydro-insulating products that can be applied on the stone surfaces that help to reduce the water infiltrations and maintain the aesthetic aspect, the most sensitive part of this problem happens almost always among the joints poorly filled out or filled out with inadequate products. This situation originates that the raining water may penetrate in the facade, leaching the cementitious material, dissolving salts, dragging them to the surface (usually in calcareous stones) and originating saline efflorescence (usually filling out the spacing joints).

9.5.2 Indirect Fixing Systems

Despite the fact that direct fixing systems are for the great majority of stone applications, the most common settling technique, there are other methods that should be stated (Fig. 9.21) such as the indirect methods.

The advantages of indirect fixing systems are clearly identified and are predominantly related with a decreased possibility of water infiltrations and humidity absorptions. Contrarily to the direct fixing systems, stone slabs are anchored with certain specific air gap (approximately 4 cm, but might vary according to system specifications) from the building wall (masonry or concrete) and this cladding construction technique is identified as a ventilated façade [23, 24].

Ventilated facades represent nowadays one of the most preferred cladding solutions, not only for new facades but also for rehabilitation. Ventilated facades are considered one of the most suitable solutions to improve buildings' thermal behaviour, reducing energy consumption required for indoor heating together with excellent functionality and protection against external agents.

To describe all the anchoring possibilities of indirect fixing systems, it is important to clarify basic principles related with ventilated facades or rainscreen systems (Fig. 9.21). They are generally comprised of:

- A visible outer skin that forms the first barrier against rain and that can be made of stone slabs or other suitable material like glass, ceramic, terracotta, aluminium or steel, among many other possibilities.
- An air gap providing ventilation that prevents water ingress into the building. In order to allow the air to circulate, openings at the base and at the top of the facade are necessary to exist. If the facade is not continuous and if it is divided into different sections, there must also be openings at the bottom and the top of each different section, as well as in the spaces for doors and windows.
- A backing wall that forms an effective air barrier and frequently includes an insulation layer. Backing walls might be made of masonry, concrete, supporting blocks or even prefabricated structures. Slabs that constitute the outer skin must always be anchored with non-corrosive metallic elements directly to the backing wall (in the case of the dowel-hole fixing systems) or first to an intermediate structure that is fixed to the backing wall (in the case of other fixing systems).

For the anchorages engagement cuts and holes are accomplished in accordance with the type of anchor (Figs. 9.22 and 9.23). The most used cut shapes are:

- Kerf cut for angles or double T support.
- Slot cuts for discs support. Normally each disc bears two plates if they are performed in the vertical edge; when the slots are made in the horizontal edges, the self-weight is distributed in two disc anchors for each stone.
- Hole for dowel insertion.

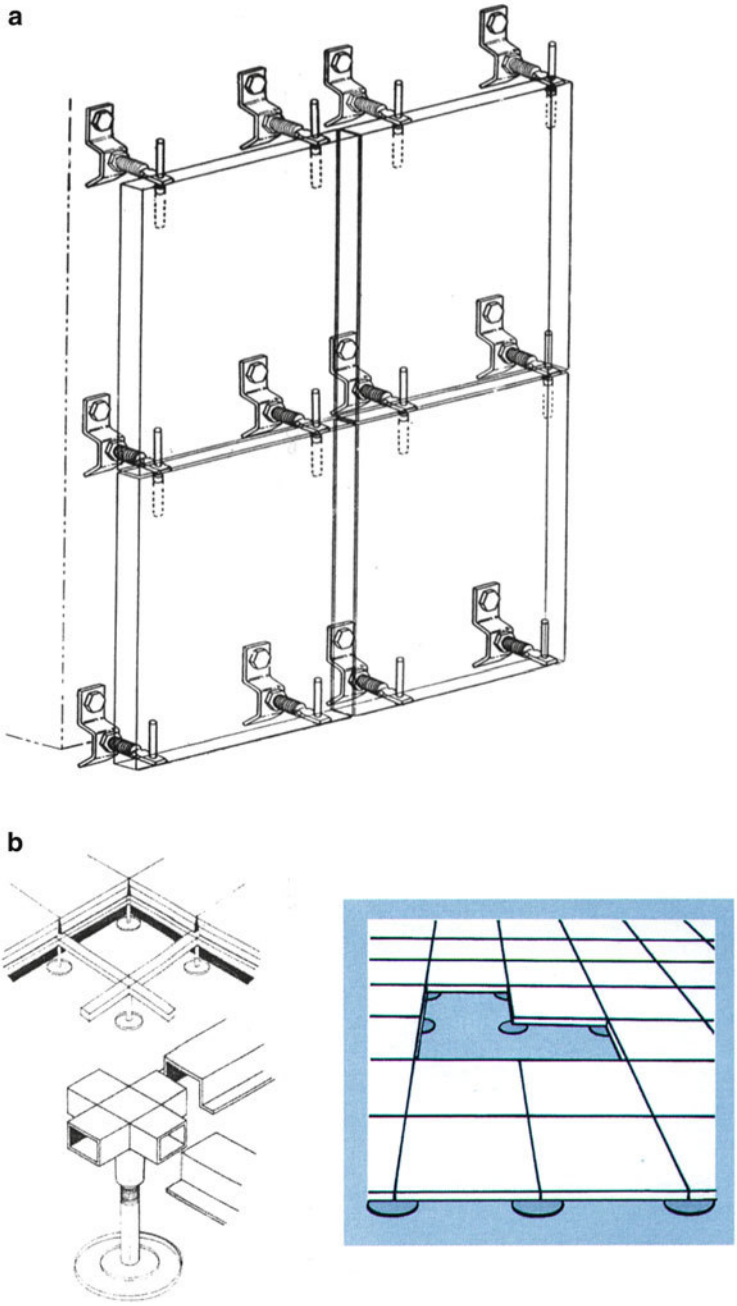

Fig. 9.21 Usual indirect fixing systems: (**a**) cladding fixing systems; (**b**) elevated floor fixing system [1]

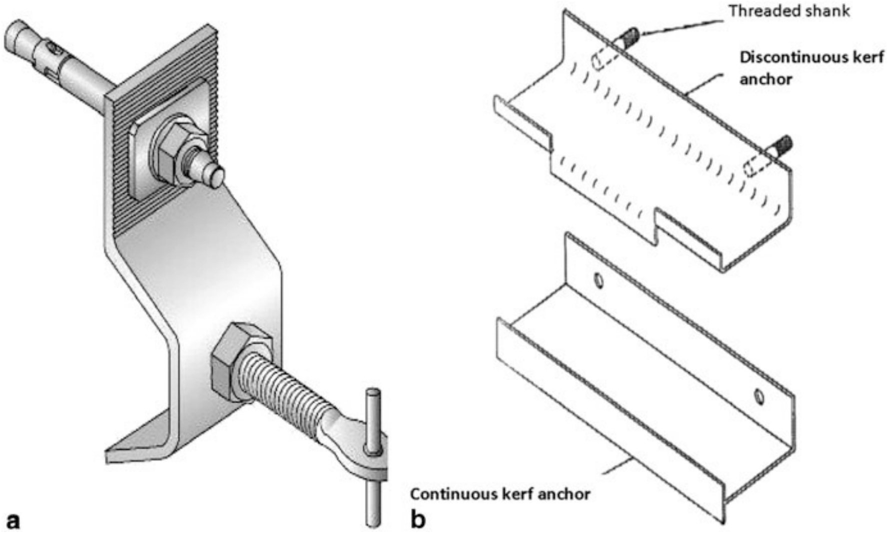

Fig. 9.22 Metallic anchors for cladding systems: (**a**) dowel-hole system; (**b**) kerf anchor system. Adapted from [23, 24]

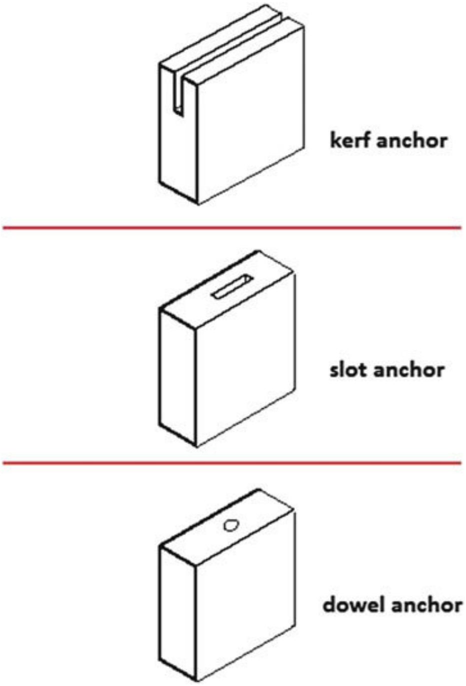

Fig. 9.23 Cut shapes in dimension stones for mechanical anchorage [23, 24]

Figure 9.24 identifies the most common solutions for application of systems with hole and dowel support. The most general case consists of vertical surfaces cladding but the horizontal cladding is often used. Special attention should be taken to the rods disposition. The rods should be always in number of four, two for edge, in case of horizontal as in vertical plates. To each rod can correspond one or two dowels. The load due to the self-weight is always associated to the two inferior dowels in any of the dispositions—dowels in the vertical boards or in the horizontal boards.

To avoid complex overstress states due to the hole misalignment, it is not recommended to have more than two holes for edge. The main issues related to

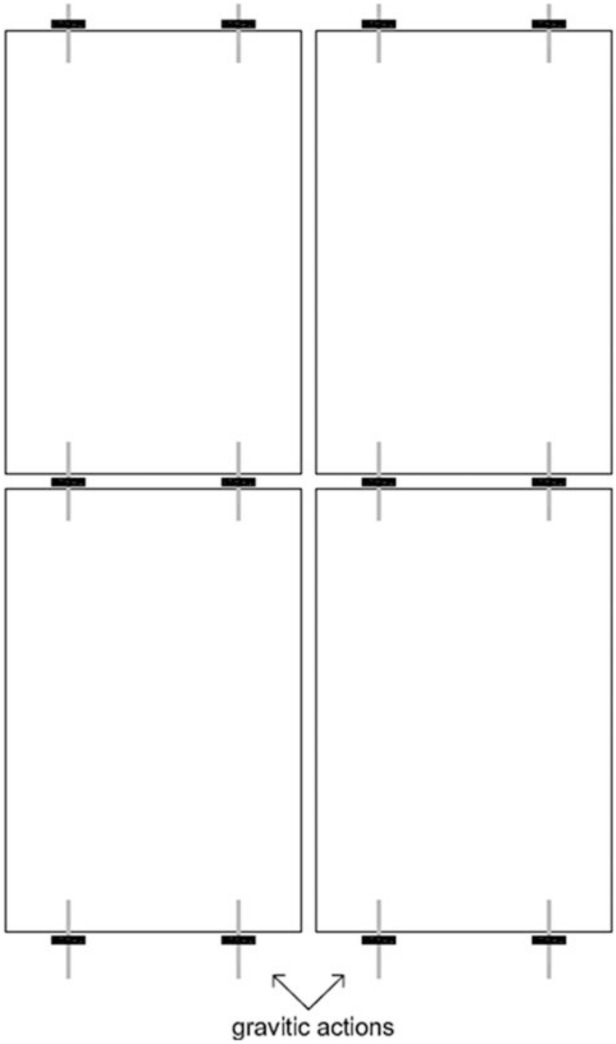

Fig. 9.24 Dowel-hole anchor system example in a facade. Adapted from [23, 24]

the rising of stone panels using dowel anchor must envisage specific considerations that are implicit in the design, such as minimising eccentric weight on anchorage and preventing slip of the connection after vertical adjustment with diagonally slotted washer plate; using horizontal slot to align dowels with holes; placing plastic or metal adjustment bearing shim slightly larger than anchor's fastened face; placing plastic or stiff rubber shim for levelling, separation and to prevent bearing of stone dowel weld; minimising hole depth, including variances and tolerances; locating hole in the centre third of panel thickness; and maintaining clearance to avoid point loading on dowel end, to avoid dowel misalignment in hole and resulting prying on stone panel, among others.

Nowadays several other fixing systems exist. One of them is the undercut fixing system. This anchoring type is characterised by a special expansive head forged on the end of a threaded shank which fits. Mechanical engagement occurs when the special headed or tooled rod fits into a contoured groove, routed into the stone with a high-speed custom diamond tool into a matching slot in the backside of the stone slab (Fig. 9.25).

Stone panels are fixed in four points in the backside of the slab. This type of anchor promotes higher pull-out resistance compared, for example, with slabs fixed with dowels inserted in the edge of the stone slab. Since bending strength is reduced by 50 % (compared with dowel anchorages), these anchors allow to reduce stone slab thickness and to increase slab dimensions.

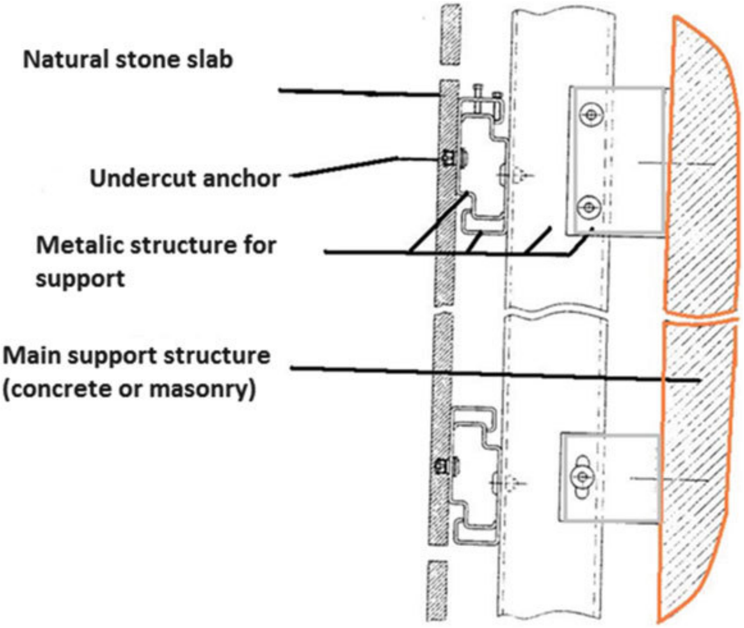

Fig. 9.25 Undercut fixing system. Adapted from [23, 24]

After mechanical engagement of the anchors, threaded shanks are tightened to angle bars, normally made of aluminium. After this, angle bars are fixed and adjusted to metallic horizontal bars (intermediate structure/supporting frame) which are fixed to the backing wall of the building.

This type of anchorage allows excellent manufacturing and setting times, when compared for example with dowel anchoring. Undercut anchoring allows tripling typical stone installation production rates because the individual stone adjustment is virtually eliminated due to the pre-alignment accuracy of the anchoring system. This anchoring system is still considered one of the most expensive available in the market and it is predominantly used in the USA, Canada and also in the UK and Germany.

9.6 Conservation, Durability and Maintenance of Stone Construction Products

Stone is a material that has been processed by nature and as a consequence of its geology many uncertainties might influence its mechanical behaviour as a cladding material. Stone chemical composition, mineralogy, petrography, texture, physical and mechanical properties, action of external agents and different exposures, variabilities of the anchorage components (or geometry), support systems themselves, etc. might contribute independently to the uncertainties that influence mechanical resistance.

Stone durability changes depend usually on more causes than just mineralogy (stone alterability). Climate, environmental and human factors or facade architectural issues are just examples of aspects that might influence stone durability. Several times in practical cladding applications, many agents such as temperature, moisture, pollution or salt might be present which makes the results interpretation harder.

Stone durability is usually more affected in urban environments. Usually changes in colour, stains, efflorescence and material loss are common aspects of stone materials decay.

In order to avoid problems, stones should be carefully tested and durability tests are available for decay evaluation. However, there are criticisms concerning durability accelerated ageing tests due to its poor relationships to natural decay processes. In fact, in our opinion, these tests should be repeated for each new batch or each new decay conditions. If a certain stone was successfully applied on a similar project in the past, it might not present the same behaviour on a different project.

One of the recommended procedures for stone building conservation is the periodical maintenance (each 2 years) to evaluate if any visual changes occur. Then every 5 years a complete inspection may be done using non-destructive methods such as ultrasound (among other methods).

Regarding conservation, one of the most common measures that should help to maintain the aesthetical feature of the stone material is cleaning. However it looks like simple task, it should be mentioned that it is necessary to take into account each

Table 9.9 Main cleaning techniques used for stone maintenance [1]

Cleaning technique	Brief description
Water jet cleaning (high and low pressure)	Suitable for soft stone types. Usually followed by brushing to clean any details and freshwater cleaning
Air jet cleaning with abrasive	Highly aggressive technique. It should be used with caution. This technique is noisy and produces a large quantity of harmful particles. Recent methods are evolving to reduce particles and increase productivity
Water jet cleaning with abrasive	Cleaning technique similar to the previous one but with low health impact because it uses water. It is also possible to use special abrasive materials that can work at lower pressures
Cleaning with chemical agents	Chemical products are applied of the stone elements after previous preliminary tests. This product application should be done after the control of several factors such as Ph and acting time
Cleaning with laser	One of the most recent cleaning processes. Usually more suitable for heritage works. Laser techniques are based on micro-resonance leading to superficial detachment of crusts and stains
Other cleaning processes	There are several mechanical processes that allow stone abrasion such as brushing or abrasive discs. However many of these methods are quite aggressive and may compromise stone materials integrity. When used these methods should work at a level in which they do not harm or stain the stone materials

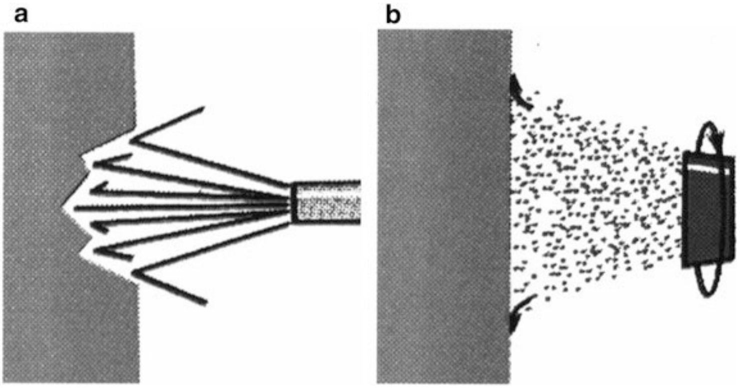

Fig. 9.26 Stone cleaning with air jet with abrasive: (**a**) high wear abrasion during the cleaning process; (**b**) low wear abrasion during cleaning process [1]

material characteristic. If the cleaning technique is not suitable, permanent damages may occur. It is expected that some of the stone features become clearer after cleaning. If so, repair works with suitable mortars should be made.

It is possible to divide the cleaning techniques in two categories: physical and chemical. Both types are used at the same time or separately. Table 9.9 shows the main cleaning techniques and a brief description of each method. In Fig. 9.26 two stone cleaning techniques are depicted.

9.7 Life Cycle

In general, the life cycle of a rock can resemble its own genesis. Rocks are formed by several minerals that are consolidated for millions of years due to several natural actions and earth mechanisms. On the other hand, these minerals are originated by natural processes such as the rock erosion, magma crystallisation within the earth's crust or from the expelling materials from a volcano. In this sense, the life of a rock does not have a definitive end, just a time where the application where the stone product is employed has reach its end.

In the last centuries, and at least 50 years ago, the main construction solutions employed in countries like Portugal were mixed [12]. The builders employed stone as the main structure (or adobe bricks where stone was not easily found), whereas the pavement and light roof was made of wood. This situation allowed the use of stone in a long term, taking into account that buildings were supposed to last during tens or even hundreds of years always accomplishing the same function.

With the increase of concrete, worldwide building solutions evolved radically, imposing the use of armed concrete or other solutions involving cementitious materials. Yet, the overall weight of a modern building is very similar to that of 50 years ago. And, although there is some belief that the building structural resistance has slightly increased, we watch a truly regression in the environmental impact of today's methods [12]. With some exceptions (easier to recycle and lowering the combined building's weight), the introduction of industrial concrete components in a non-uniform way (usually combined with other materials) has decreased substantially the recyclability of modern solutions. Most of these solutions denote also a tremendous difficulty in achieving good acoustic and thermal insulation behaviour, which is contrary to what should be thought as building in the future. The energy cost consumed by buildings (6–20 % of the overall world energy consumption in the next 50 years) and the dismantling, treatment and transport cost of residues, when reached the end-life of a building, are obligations from the next architectural and engineering designers.

The activity related to energy savings will be the driver for finding the best/optimum solutions that, in 50 years, must also be renewed or recycled without endangering the environment more than they saved. The modern construction methodologies show very complex life cycle, some with too much high energy cost embedded when related with the given function. In this sense the increased use of local materials shows low transformation that implicates by itself a reduction of environmental impacts [25].

Stone, namely the product used in the construction sector, has suffered industrialisation processes aiming normally a reduction in weight, reduction of residues normally caused by cutting processes and reduction of waste caused by non-valorised materials when transformation phases are conducted. New solutions for fabricating products from stone originate stone composites such as new thin slabs (thickness lower that 0.5 mm) reinforced with polymer [26]. Nowadays, one of the solutions with more value in the market is the agglomerated stones, allowing to prove viability in the use of both residues and waste caused by stone. The current stone agglomerates were created between 1950 and 1980. Some are known as "momorito" and "terraza". The more recent developments on the polymer industry was determinant for performing some technological evolution regarding the production equipment that allows manufacturing stone composites incorporating a very high level of petreous components (calcareous and silicates). These materials have a very similar aesthetic texture when compared with natural stone and show a range of properties that allows to cover a significant number of applications (from interior to, more recently, exterior facade applications). Both natural and agglomerated materials should be considered from the same origin (despite from

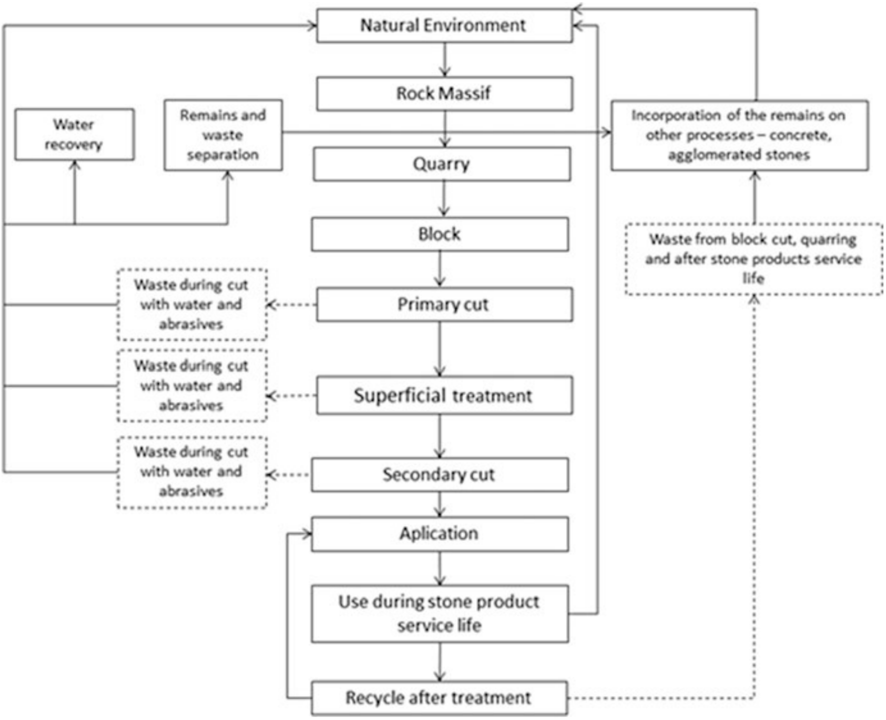

Fig. 9.27 Possible interrelations for the life of a stone product that may represent its life cycle: examples employed in products like tiles with standard dimensions

the latter having a relevant level of polymer). If used rationally, these materials contribute favourably to our environmental sustainability.

As it is easy to verify, it is not simple to approach the life cycle of petreous materials without a more vast approach. Despite this fact, an attempt to analyse life cycle of a stone product can be observed in Fig. 9.27, where all meaningful interrelations are shown.

References

1. Casal Moura A (2000) Granitos e Rochas Similares de Portugal, ed. I. G.e. Mineiro, Porto, p 179
2. Guerra Rosa L, Amaral PM, Anjinho CA, Cruz Fernandes J, Antunes SD, Antunes J (2000) Ornamental stone processing—new methodologies for the characterisation of petreous materials and diamond tool behaviour. In: 2nd International Conference on Ornamental Stone, Vila Viçosa, Portugal
3. Guerra Rosa L, Cruz Fernandes J, Amaral PM (1998) Method for classification of stone materials according to their abrasiveness. In: Proceedings of EUROTHEN'99 workshop—European Commission—industrial and materials technologies programme, Athens
4. Casal Moura A (2001) O Granito na Construção Civil e na Arquitectura: Requisitos Técnicos dos Produtos. Rochas & Equipamentos (n.61):14–44
5. Ruffa N (2001) A matter of urban maintenance. Urban fixtures: the durability and reliability of stone materials. Marmo Macchine International, pp 114–130.
6. Amaral PM, Cruz Fernandes J, Midha S, Guerra Rosa L (2001) Advances on industrial characterisation of diamond tools and ornamental stones. ROC Maquina 42:22–25
7. Philpotts AR (1989) Petrography of igneous and metamorphic rocks, Porspect Heights, IL: Waiveland Press
8. Moorhouse WW (1964) The study of rocks in thin section. John Weatherhill Tokyo, New York; printed in Japan: Harper & Row
9. Artigo do (2010) Global Stone Congress, Porspect Heights, IL: Waiveland Press
10. Primavori P (2000) The colors of stone. Marmo Macchine International, pp 22–57
11. Casal Moura A (2001) A Pedra Natural Ornamental em Portugal—Nota Breve. Boletim de Minas 38(3):161–177
12. Carvalho J, Manuppella G, Casal Moura AA (2002) Calcários Ornamentais Portugueses, Rochas & Equipamentos (n.67):6–46
13. Frisa Morandini A, Miramonti C (2003) European Standards and CE Marking on stone construction products. In: Congresso Internacional de Pedra Natural, Arquitectura e Construção, Lisboa
14. Associação Brasileira de Normas Técnicas (1995) Conheça a ABNT, 2ª edn, Rio de Janeiro, ABNT
15. NP EN 45020 (2001) Normalização e Actividades Correlacionadas. Vocabulário Geral (Guia ISO/IEC 2:2004)
16. OSNET OaDSN (ed) (2003) State of the Art in characterisation methodologies and standards, ed S.C. Sector
17. Moura AC (2006) Qualidade Industrial e Marcação CE, Março
18. NP EN 45011:2001 Requisitos para organismos de certificação de produtos
19. http://www.ce-marking.org and http://ec.europa.eu/enterprise/newapproach/standardization/harmstds/reflist/construc.html
20. Morandini AF (2004/2005) Finished products, market and characterisation: an introduction, Osnet edn, vol 15, pp 1–11

21. Correia C (2003) Patologias Identificadas e Caracterizadas em Revestimentos Exteriores de Pedra Natural com Fixação Directa. Algumas Recomendações para a sua Prevenção, Rochas & Equipamentos (n.71):21–32
22. (2000) Revêtements de murs extérieurs en carreaux céramiques ou analogues collés au moyen de mortiers-colles. Cahier des Prescriptions Techniques d'exécution, *CAHIERS DU CSTB*, Cahier 3266, Octobre
23. Camposinhos R, Amaral P (2007) Caderno Técnico de aplicação, uso e manutenção de rochas ornamentais; desenvolvido por FrontWave, Engenharia e Consultadoria, S.A., Edição Assimagra, 1° edição
24. Camposinhos R (2005) Métodos e Técnicas de Construção I—Revestimento de Fachadas em pedra natural; Instituto Superior de Engenharia do Porto—Departamento de Engenharia Civil, Novembro
25. Mendonça P, Bragança L (2002) Construção em Pedra e Conforto Térmico—Implicações na Redução do Impacto Ambiental. Rochas & Equipamentos (n.65):6–29
26. ano (2003) Construir con Granito. ROC Maquina (Abril):54–63
27. Anjinho CA, Pinto S, Pires V, Rodrigues R, Amaral PM (2006) Inovação no Sector das Rochas Ornamentais: desenvolvimento de técnicas avançadas de caracterização de materiais e produtos, ferramentas e matérias-primas, máquinas e sistemas de produção, Rochas & Equipamentos (n.84):50–62

Polymers in Building and Construction

10

António Correia Diogo

Abstract

Polymers are materials with increasing utilisation as engineering materials in the last 40 years. The building and construction industry is responsible by more than 20 % of plastics consumption in Europe (commodity and engineering thermoplastics). Thermosets also present an increased utilisation as reinforcing and structural materials, focused in structures where reduced weight and tight time frame are relevant exigencies.

This chapter provides an introductory presentation of the most relevant polymer materials from the point of view of its applications in engineering, with particular focus in building and construction industry. The relationships between structure and performance as well as a set of important material properties of the most relevant polymer materials are provided.

Keywords

Polymers • Thermoplastics • Thermosets • Polyethylene • Polypropylene • Polyvinyl chloride • Polystyrene • Polyurethanes • Elastomers • Polymer testing • Physical testing • Dynamic mechanical analysis

10.1 Introduction

The first materials containing polymers used to build shelters or houses were probably wood and thatch. Wood and thatch are made up of natural polymers: cellulose and lignin, among others. Wood is still used as a "structural material" in main walls, flooring, pillars, beams and rafters, and thatch is used as a "functional

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M.C. Gonçalves, F. Margarido (eds.), *Materials for Construction and Civil Engineering*, DOI 10.1007/978-3-319-08236-3_10

material” in roofs and coverings, for dividers, etc.. Even now, wood represents 7.6 % of the total (weight) of materials consumption in building and construction industry, for Western Europe.

Polymers (including cellulose and lignin) are macromolecules, i.e. big molecules made up of chains of smaller molecules, the *monomers*, chemically bonded together. Etymologically, monomer comes from the Greek “μόνος + μερῶς” (*monos* + *meros*), meaning “one part”. Polymer comes from “πολύς + μερῶς” (*polys* + *meros*), meaning “many parts”.

Cellulose and lignin are natural or biological polymers; they are polymers synthesised by living plants to perform one or more given biological functions. Living organisms developed the ability to produce an enormous range of different macromolecules, by combining a scarce number of chemical units. Twenty amino acids are enough to build more than ten million different proteins that are estimated to exist; a few more than 20 monosaccharides (sugars) are the building monomers of the hundreds of existing polysaccharides or glycans. For nucleic acids, a 5-carbon sugar (ribose or deoxyribose), a phosphate group and five different nitrogen bases are enough as building blocks.

About two centuries ago, *Homo sapiens* started trying to do the same in chemical factories, and he was successful: synthetic polymers were born. At first, several polymers were produced from molecules of natural origin. In 1839, vulcanisation of poly-isoprene, extracted from the resin of *Hevea brasiliensis* (rubber tree), led to the first synthetic elastomer: vulcanised natural rubber. The search for substitutes of ivory, the raw material for billiard balls, impelled the invention of the first thermoplastic, the celluloid, in 1863; the raw materials for celluloid were nitrocellulose and camphor. Elephants gratefully acknowledged the invention of celluloid. Celluloid found also application in photography and movie films, ping-pong balls and so on. The search for substitutes for natural silk began *circa* 1880: the first one was *rayon* (regenerated cellulose fibres) made from viscose (cellulose xanthate) and cellophane.

The first totally synthetic polymer to be manufactured was *Bakelite*. Bakelite is a thermoset polymer, made by cross-linking a phenol formaldehyde resin. It was developed in 1907 by Leo Baekeland and produced since 1910.

It is interesting to remark that, 50 years before the beginning of Bakelite production, the synthesis of thermoplastic oligomers at the research laboratory of Charles Wurtz, in Paris, was reported. Between 1859 and 1861, Agostinho V. Lourenço (1822–1893) synthesised a series of oligomers he called *ethers composés du glycol* (“composed ethers of glycol”) and *alcohols polyethyleniques* (“polyethylenic alcohols”). Today, they are named as polyethylene glycol or poly (oxyethylene); the high-molecular-weight counterparts are known as poly(ethylene oxide).

Polymer materials started to be manufactured as substitutes for more expensive materials. They were established quickly on the market, and soon they got their own place as first choice materials for a large number of applications. The main benefits are:

- *Lightweighting*—They make possible the design and build-up of lighter structures and objects, with improved performance, and at lower costs (per unit of weight).
- *Processability*—In general, they are easily moulded and shaped (as the name "plastic" suggests) by heating at relatively low temperatures (50–250°C), as compared to metals or ceramics.
- *Durability*—Polymers have good resistance to adverse environments, do not suffer electrochemical corrosion, and can keep their properties unchanged for a long time.
- *Versatility*—It is relatively easy to select, modify and adapt polymer properties according to specific needs or requirements.
- *Economy*—In general, the use of polymer materials has a positive effect in cost reduction: raw materials costs, manufacturing (processing) costs, maintenance and operational costs.
- *Competitiveness*—For the same application and for similar performance, plastic products are generally cheaper.
- *Environmental advantages*—Polymer materials present very often the best cost-benefit ratio when evaluating the environmental costs associated with the full life cycle of products. It is estimated that polymers also help in reducing environmental costs in transport (45 %), electricity consumption (42 %), feedstock consumption (4 %) and others (9 %).
- *Recyclability*—In general, polymers can be recycled. In the last 20–30 years, polymer recycling was successively incorporated in current polymer industry activity. For polymer materials used in specific applications (e.g. car plastic fuel tanks, PET bottles, . . .), closed loop recycling has been implemented and expanded. Also a number of new raw materials and innovative products are being currently developed from polymer recyclates.

10.2 Polymer Structure

Polymers are macromolecules consisting of repeating chains of smaller molecules, the *monomers*, connected by chemical bonds. Any molecule having two or more reacting groups (bi- or poly-functional) is a good candidate for a monomer. In addition to the variety of monomers available for polymerisation, it is further possible to control the polymerisation reactions in many ways. When a given monomer is polymerised (by one or a sequence of chemical reactions), different output variables are to be considered:

1. *Chain length*: The number of monomers that form one chain is called the *degree of polymerisation*; its value depends on the way the polymerisation proceeds.
2. *Chain topology*: The topology of polymer chains can be controlled during polymerisation: either *linear* or *branched* chains can be produced. *Branches* are sub-chains connected to the linear main chain, at some places called *branch points*.

Branching can give rise to major changes in properties and performance of polymers. Polyethylene is one of the best examples: *short-chain* and *long-chain branches* strongly affect material properties and material functions in different ways.

It is not always possible to difference main chain and branches in macromolecules; if so, macromolecules look as a set of linear sub-chains assembled in some given way. Some examples are (see Fig.10.1):

- *Ladder polymers* consist of two parallel chains interconnected by smaller sub-chains in regular intervals.
- *Comb polymers* are constituted by an array of sub-chains grafted in one main chain.
- *Tree polymers* are also constituted by a main chain with a digit number of grafted sub-chains; in tree polymers, the grafted sub-chains are themselves branched chains (as in a tree). This feature enables the distinction between tree polymers and branched polymers.
- *Star polymers* are constituted by a digit number of sub-chains, the "arms", connected to a common core.
- *Dendrimers* may be considered as star polymers where the arms are constituted by tree polymers. Dendrimers are obtained when star polymers (first-order branching), with multifunctional ends on the arms, add additional sub-chains (second-order branching). If the sub-chains have also multifunctional ends, they may add additional sub-chains (third-order branching). By this way, different orders of branching can be produced; the number of chain ends (terminal groups) increases in an exponential way with the maximum order of branching.
- *H-polymers* are constituted by five sub-chains bound at two points, as in uppercase H.

3. *Crystallinity*: On cooling, chain monomers may become spatially organised in a regular way at given places, and crystallisation proceeds; otherwise, a glassy polymer is formed. In both cases, the final morphology depends on the way cooling was done. The volume fraction of crystallised material is called the *degree of crystallinity*; its value is manageable in several cases.
4. *Cross-linking*: Polymer chains (or sub-chains) can also form networks of *cross-linked chains*. The mesh size of the network is related to the *degree of cross-linking* (the number of cross-links per chain), to the *cross-linking density* (the number of cross-links per unit volume) or to the sub-chain length, given by the *molecular weight between consecutive cross-links*; the three quantities are related one another. The mesh size of the network increases as the number of monomers between consecutive cross-links decreases. Vulcanised rubber is an example of a low mesh, loose polymer network (low degree of cross-linking, many monomers between consecutive cross-links). Thermoset polymers (after cure) are an example of very tight cross-linked chains (high degree of cross-linking, very few monomers between consecutive cross-links).

Homopolymers are constituted by identical monomers. Nevertheless, their properties can be modified within wide limits by changes in the degree of

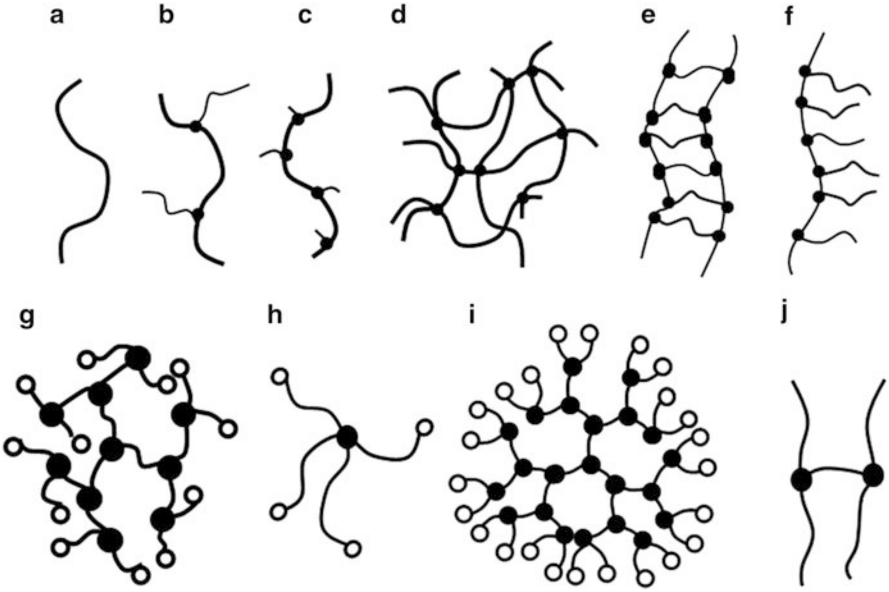


Fig. 10.1 Chain topology of polymers: (**a**) linear chain; (**b**) long chain branches; (**c**) short chain branches; (**d**) network of crosslinked chains; (**e**) ladder polymer; (**f**) comb-like polymer; (**g**) tree-like polymer; (**h**) 4-arms star polymer; (**i**) dendrimer; (**j**) H-polymer. *Full circles*: branching points. *Open circles*: end chains

polymerisation, changes in the degree of crystallinity, changes of the amount of branching and changes of the length of branches of the main chain. Such changes make it possible to adjust the properties ("to set the grade") of the resulting homopolymer material to a wide range of uses and requirements. Polyethylene is one such example.

Polymerisation may also involve more than one kind of monomers.

Copolymers are polymer chains produced by polymerisation of two or more different monomers. The order and arrangement of the different monomers that make up a copolymer can also be set as follows:

- *Alternating copolymers*—monomers A and B are arranged alternately in the chain: ABABABABABABABAB.
- *Block copolymers*—monomers A, B and C are organised into two or more blocks of identical monomers: di-blocks like AA(. . .)AA-BB(. . .)BB, tri-blocks like AA(. . .)AA-BB(. . .)BB-CC(. . .)CC and so on.

  Example: triblock copolymers of styrene-butadiene-styrene (SBS)
- *Random copolymers*—monomers are randomly arranged in the chain. For instance,

  AABABBBBAABAAAA.

  Example: ethylene-propylene-diene copolymers (EPDM).

With few exceptions, polymers cannot be processed just as obtained at the reactor exit ("fluffy polymers"). Fluffy polymers need to be combined with other substances before processing. The designation of such procedures varies with industrial sector: thermoplastic and thermosetting polymers are *compounded*; rubbers, adhesives and inks are *formulated*; textiles are *finished*. Compounded thermoplastic and thermosetting polymers (before cure) are called *resins*. Resin is, in some sense, a utilitarian name based on the fact that molten thermoplastics before processing, thermosetting polymers before cure and coniferous resins look and flow in a similar way.

Compounding may include mixing with:

- *Additives* (pigments or dyes, flame retardants, heat stabilisers, lubricants, antioxidants, anti-static agents, etc.). They are used in small proportions (<5 %) for changing specific properties other than mechanical properties.
- *Modifiers* are added in greater proportions and do affect mechanical properties. Examples are *fillers* and/or *reinforcements*, such as mineral particles and glass fibres.
- *Other polymers*: The particular designation of such mixing is material dependent. Thermoplastics are *blended* with thermoplastics, *toughened* (impact-modified) with rubbers and *reinforced* with fibres. Rubbers are *mixed* with fibres and *blended* with other rubbers. Thermosets are *reinforced* with fibres. *Polymer alloys* are special polymer blends, looking homogeneous and with controlled morphology in a reproducible way.

In general, different polymers are not thermodynamically miscible: few exceptions are known. Here "thermodynamically miscible" or "miscible in thermodynamic sense" means that, after mixing, one single homogeneous phase in thermodynamic equilibrium is produced. Low-molecular-weight substances are miscible quite often; for example, water and ethanol (ethyl alcohol) are thermodynamically miscible. Egg and olive oil are not thermodynamically miscible: if they are put together, three phases are obtained: olive oil, egg white and egg yolk. Nonetheless, by mechanical action ("blender"...) and by inducing changes in surface tension (egg yolk lecithin and added mustard....!), it is possible to get a product homogeneous to the naked eye: it is the emulsion called "*mayonnaise*". With the aid of a microscope, one can easily check that immiscibility remains at microscopic level.

Polymer blends may be divided into:

- *Miscible blends* (thermodynamically miscible)
- *Immiscible blends* (thermodynamically immiscible)
- *Polymer alloys* (thermodynamically immiscible, visually homogeneous, with controllable and reproducible morphology)

The difference between immiscible blends and polymer alloys is that polymer alloys look visually homogeneous, and their morphology can be controlled in a reproducible way. Morphology is set up by adding one or several "*compatibilisers*"; "compatibilisers" act like surfactants reducing the interfacial tension and improving

Table 10.1 Dispersed systems

Continuous phase Dispersed phase	Solid	Liquid	Gas
Solid	Solid sols	Suspension	Smoke
Liquid	Sol	Emulsion	Fog
Gas	Solid foam	Foam (liquid)	–

the dispersion. "*Compatible blends*" is a utilitarian term for immiscible blends that look transparent to the naked eye.

Polymer blends and alloys are examples of dispersed systems, not necessarily composed of liquids, in which one component (the "dispersed phase") is dispersed in the "continuous" phase formed by the other component.

A general classification of dispersed systems is presented in Table 10.1.

10.3 Classes of Polymeric Materials

World plastics consumption (thermoplastics, thermoset resins and composites) was 260 million tonnes (Mtonne) in 2007, 100 Mtonne in 1989 and only 1.5 Mtonne in 1950. For 2015, the expected world plastics consumption is very close to 300 Mtonne: about 270 Mtonne for thermoplastics, 30 Mtonne for thermosets. If the rubber (elastomers) consumption is included (about 30 Mtonne), the world polymers consumption expected for 2015 is 330 Mtonne.

The European consumption accounts for about 21 % of the world plastics consumption (57 Mtonne in 2012). In terms of applications, the distribution by the different market segments in 2012 was:

- 39.4 % for packaging
- 20.3 % for building and construction
- 8.2 % for automotive industry
- 5.5 % for electrical and electronics applications
- 4.2 % for agriculture
- 22.4 % for other sectors (appliances, household and consumer products, furniture, sport, health and safety products)

Table 10.2 shows the relative amounts by resin type for commodity and engineering plastics.

Currently, there are considered six different classes of polymer materials:

1. *Thermoplastics*: Thermoplastics represent almost 80 % of the world consumption of polymers. They can be moulded and shaped by heating, several times. Thermoplastics are normally split into (see Table 10.3):
   (a) *Commodity plastics* are general-purpose thermoplastics, produced on a large scale. They include high-density polyethylene (HDPE), low-density polyethylene (LDPE) and linear low-density polyethylene (LLDPE),

Table 10.2 Plastics demand in Europe by resin type (2012)

Commodity plastics	%
LDPE/LLDPE	17.4
HDPE	12
PP	19
PVC	10.5
PS/EPS	7.5
PET	6.6
Engineering plastics	
PUR	7
Others	20

Note: Polyurethanes (PUR) include a wide range of polymers (thermoplastics, thermosetting materials, elastomers, fibres) that have in common the existence of a functional urethane (or carbamate) chemical group in their structure

Table 10.3 Classes of thermoplastics

Thermoplastics	Commodity plastics	Polyethylene	PE
		Polypropylene	PP
		Polyvinyl chloride	PVC
		Polystyrene	PS/EPS
		Polyethylene terephthalate	PET
	Engineering plastics	Polybutylene terephthalate	PBT
		Aliphatic polyamides	PA
		Styrenic copolymers	ABS/ SAN
		Vinyl copolymers	
		Polymethyl methacrylate	PMMA
		Acrylics	
		Polycarbonate	PC
		Polyacetal	POM
		Poly(*p*-phenylene oxide)	PPO
	High-performance engineering plastics	Polytetrafluoroethylene	PTFE
		Polyarylates	PAR
		Aromatic polyamide	PAA
		Polyimides	PI
		Polyamide-imide	PAI
		Polyetherimide	PEI
		Polyetherketone	PEK
		Polyether ether ketone	PEEK
		Polyethersulphone	PES
		Polyarylsulphone	PAS
		Poly(*p*-phenylene sulphide)	PPS

polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS) and expanded polystyrene (EPS), and polyethylene terephthalate (PET).

   (b) *Engineering plastics* are thermoplastics that exhibit improved properties such as mechanical strength, heat resistance, chemical stability and dimensional stability as compared to commodity plastics. Engineering plastics include polyesters like polybutylene terephthalate (PBT), aliphatic polyamides (PA) also called *nylons*, polymethyl methacrylate (PMMA), polyacetal or polyoxymethylene (POM), styrenic and vinyl copolymers, poly-*p*-phenylene ether (PPE), polyurethane (PUR) thermoplastics and polytetrafluoroethylene (PTFE, Teflon).
   (c) *High-performance engineering plastics* include advanced engineering plastics that exhibit outstanding properties and superior performance: high temperature resistance, high tensile strength, high impact resistance, etc. They are more expensive than engineering plastics. They include polymers such as polyarylether-sulphones (PSU, PES, . . .), polyphenylene sulphide (PPS), aromatic polyamides, polyaryletherketones (PEK, PEEK, . . .), polyimides (PI) and polyamide-imides (PAI).

2. *Thermosets*: They are cured thermoset polymers which networks of tightly cross-linked chains. They are easily mouldable before *cross-linking* (*curing*) occurs; once the cure is complete, the shape is kept forever. The matrix for the vast majority of polymer-based composites is built by cross-linked thermoset resins.
3. *Elastomers*: This designation includes natural rubber and its synthetic substitutes. Natural rubber still represents about 40 % of the elastomers market. Elastomers behave like cured (vulcanised) natural rubber. Elastomer resins are easily mouldable and poured before cure. It is worth mentioning that, cure is often called “vulcanisation” even when sulphur is not present. Elastomers *sensu stricto* (cured elastomer resins) are constituted by low mesh networks of cross-linked chains. Elastomers present three peculiar characteristic properties: flexibility, deformability and resilience. *Flexibility* is related to cross-link density: the values of Young’s modulus are of the order of magnitude of 0.1–10 MPa. *Deformability* of elastomers is very high: they can be stretched up to more than three times the initial length, without rupture. In some cases, the stretch ratio may be as high as 10 or even more. *Resilience* means that the elastomer is able to recover the original shape after being stretched. *Sensu stricto*, resilience is defined as the ratio between the elastic energy released at elastic recovery and the elastic energy absorbed during deformation.
4. *Fibres*: Synthetic fibres are made from thermoplastic polymers (PP, PET . . .) by use of the appropriate processing methods (dry spinning, wet spinning, melt spinning). Fibre toughness strongly depends on the degree of crystallinity and on the orientation of the polymer chains; it is induced by stretching the spun fibre at a given draw ratio: the draw ratio is the main controlling parameter for orientation. Synthetic fibres are used in fabrics, in other textile products and as reinforcements in composites.

5. *Functional polymers*: They are polymers tailored to provide a specific function for a given application.
    (a) *Coatings and paints*: Coatings are formed of fine layers of material that aim to protect or decorate the substrate; in the latter case, they are normally referred to as *paints*. Polymeric coatings may or may not contain a volatile solvent, and the formation of the layer (film) may or may not involve a chemical reaction.
        i. *Non-reactive coatings*: These coatings are produced from polymeric waxes; some heating is usually required for easy spreading. *Lacquers* are polymer solutions, in which the formation of a film occurs after solvent evaporation. The original name referred only to alcoholic solutions of natural gums. The name "*paint*" or "*latex paint*" normally applies to latex formulations from emulsion polymerisation, mixed with pigments and other components.
        ii. *Reactive coatings with solvent*: These coatings are solutions that contain a *siccative oil* (the designation used for unsaturated poly-functional monomers), which polymerises in the presence of atmospheric oxygen to form a cross-linked polymer layer. *Varnishes* are mixtures of resins and siccative oils; *enamels* are pigmented varnishes. *Alkyd resins* ("al" from *al*cohol and "yd" from "ac*id*") are composed of unsaturated carboxylic acid esters and poly-functional alcohols; polymerisation by radical attack to the double bonds produces the coating.
        iii. *Reactive coatings without solvent*: In this case, polymerisation can be induced by a plasma discharge, through high-energy radiation, etc. *Photosensitive paints* are polymerised using ultraviolet radiation. *Photoresist coatings* are another example.
    (b) *Adhesives and sealants*:
        i. *Adhesives* are used to join two or more surfaces and to provide a certain mechanical strength to that bond. They are divided into *hot-melt adhesives*, *contact adhesives* and *structural adhesives*. *Hot-melt adhesives* are essentially constituted by molten thermoplastics which provide adhesion after solidification. *Contact adhesives* are used at ambient temperature; their formulation includes several components such as elastomers, mineral fillers, cross-linkers, solvents, colourants, rheology modifiers, adhesion promoters and other additives. *Structural adhesives* are based on thermosetting resins, which form an adhesive layer in which curing (cross-linking) occurs; formulations usually include modifiers to increase flexibility and toughness of the cured adhesive, cross-linking agents, etc. Structural adhesives play an important role in the resistance and stability of structures.
        ii. *Sealants* serve to insulate a given volume by preventing liquids or gases from penetrating that volume from outside. Unlike adhesives, sealants are only designed to comply with insulation needs and are not expected to play any structural role besides insulation. Sealants design requires a strict control of the viscoelastic material functions, since evaluation of

the final properties is done in terms of characteristics such as deformability (flexibility), modulus (or mechanical susceptibility) and elastic recovery. For example, a sealant for glass should have good elastic recovery (>40 %). Selecting a sealant for other unions depends on the type of union considered and on the expected load history: unions with little or higher mobility, joints submitted to cyclic loads, joints involving different substrates, etc.

(c) *Inorganic polymers*: The main chain of inorganic polymers does not contain carbon atoms. The best-known examples are silicones, constituted by chains of silicon and oxygen. These materials have excellent stability at high temperatures: silicone elastomers can support temperatures up to 300 °C for a long time; silicone oil, constituted by low-molecular-weight silicones, can last for a long time at high temperatures without any appreciable loss in performance.

(d) *Biopolymers/biological polymers*: The most commonly used polymers of this type are derived from cellulose.

6. *Advanced functional polymers*: This class includes highly complex and sophisticated polymers, tailored as advanced functional materials for highly demanding applications. Such applications include photonic devices, medical applications such as drug delivery systems and functional surfaces.

10.4 Polymers and Construction

Table 10.4 displays the expected demand in building materials in the United States for 2015.

In Western Europe, the building and construction industry spends about 20 % of the thermoplastics produced every year. Table 10.5 shows the way in which the almost 10 Mtonne of polymers consumed by the construction industry in Western Europe are distributed among the different polymer families.

Currently, the percentage of polymers used in a residential building is around 10 % (in weight). Among their different uses, the following stand out:

- Window and door frames, windows and blinds
- Gas, water and sewage systems
- Insulating material for electrical cables
- Bathroom and sanitary equipment
- Thermal insulation materials
- Skylights
- Flooring or coatings for flooring
- Impermeable coating for swimming pools
- Covering for swimming pools

The use of polymeric materials in the building and construction industry is mostly due to their following characteristics:

Table 10.4 Consumption of building materials in Western Europe

Materials	Mtonnes	%
Concrete	280	38.6
Concrete	250	34.5
Clay (bricks, tiles)	75	10.3
Wood	55	7.6
Iron and steel	19	2.6
Stone	18	2.5
Asphalt and bitumen	18	2.5
Polymers (2010)	9.54	0.7
Flat glass	4.8	0.7
Mineral wool	2	0.3
Aluminium	1.2	0.2
Total	7,278	

Table 10.5 Consumption of polymers in construction in 1995

	%
PVC (polyvinyl chloride)	55.3
PU (polyurethanes)	9.5
EPS (expanded polystyrene)	9.0
XPS (extruded polystyrene)	2.9
HDPE (high-density polyethylene)	7.0
LDPE (low-density polyethylene)	5.0
PP (polypropylene)	2.5
UP (urea-formaldehyde, phenolic compounds)	1.7
PC (polycarbonate)	1.5
PMMA (polymethyl methacrylate)	1.4
Amino + POM + ABS	0.7
PA (polyimides)	0.3
Total	100

- *Durability*—Generally, polymers keep their properties for a long time under a wide variety of environmental conditions: temperature, moisture, light, solvents, etc., specifically:
  - Resistance to corrosion: excellent in almost all situations.
  - Resistance to hydrolysis: excellent or controllable by using the correct formulation.
  - Resistance to light irradiation: good to excellent, if properly controlled in the formulation.
  - Hygiene and cleanliness: impurities and dirt are easily removed.
- *Reliability* and *economy*—As already mentioned, there are significant reductions in production costs (less expensive raw materials), processing, maintenance and running costs. As an example, let us look at the following data for thermal insulation:

- Thermal insulation—windows: a PVC window is an efficient thermal barrier with an expected working life around 50 years, without the need for any maintenance.
- Thermal insulation—wall: using 50 kg of thermoplastic foam in domestic thermal insulation allows savings of 3,700 L of fuel over 25 years; it is estimated that the energy consumption used to heat housing has halved in the last 20 years thanks to the use of foam thermal insulation.
- Lower weight—polymers are generally light materials; foams can have a density in the range of 20–50 kg/m^3.
- Prices are normally advantageous.
- Zero or very low maintenance costs.
- Favourable environmental impact—they allow for a substantial reduction in energy consumption, they are easily recycled and waste production can be substantially minimised by using appropriate procedures.

As an example, it is interesting to note the "three-litre house": a house designed by BASF in 2000 and measuring 100 m^2 in area, which consumes 3 L of fuel per square metre per annum. The goal is achieved by intensively using different polymeric materials. There is a brief description of the prototype in the Appendix to this chapter.

Table 10.6 shows the main applications of polymers in building and construction.

Table 10.6 Main uses of polymers in building and construction

	Material	Kilotonnes	Total
Tubing/conduits	PVC	1,329	1,922
	HDPE	341	
	PP	121	
	LDPE	88	
	ABS	13	
Insulation	PU	464	1,044
	EPS	440	
	XPS	140	
Floors/walls	PVC	343	343
Window and door frames, windows	PVC	600	600
Profiles	PVC	290	290
Carpets, rugs	PE	156	266
	PVC	110	
Furniture	PS	156	425
	UP	85	
	PC	75	
	PMMA	70	
	Amino	20	
	PA	25	
	POM	4	
Total			4,890

10.5 Properties of Selected Polymers

Tables 10.7 and 10.8 provide data on several mechanical and thermal properties for selected polymers, including comparative costs. Data about polyurethanes was not included, because of the large variability of chemical composition of the constituent monomers which brings forth a large variability of physical, mechanical and chemical properties. As a matter of fact, polyurethane thermosets present physical and mechanical properties more close to other thermosets than to thermoplastic polyurethanes; polyurethane elastomers behave more similar to other non-polyurethane elastomers than to polyurethane foams; and so on.

This section includes brief notes on the structure, composition and properties of the most widespread polymer families: PE, PP, PVC, PS, polyurethanes and elastomers.

10.5.1 Polyethylene

The name *polyethylene* covers a family of thermoplastic resins produced by *polymerisation* of ethylene (*monomer*). Ethylene is found in certain sources of natural gas, but the main source of ethylene is crude oil. Ethylene is produced in petrochemical plants by steam cracking of naphtha, liquefied petroleum gas or ethane.

Low-molecular-weight polyethylenes are liquid and are used as lubricants. Polyethylenes with molecular weight between 2,000 and 6,000 g/mol are waxes (*paraffin waxes*). Polyethylenes with higher molecular weight are solid.

The polymerisation of ethylene is done in reactors with the help of catalysts. The most common families are Ziegler–Natta catalysts, Phillips catalysts and metallocene catalysts. According to the polymerisation conditions, the molecular weight distribution can be controlled within some limits. Metallocene catalysts are particularly able to provide narrow molecular weight polyethylenes as compared to other catalysts.

Branching strongly affects the processability and the final properties of polyethylene. Polymerisation conditions may favour the grafting of long branches in the main chain (*branched polyethylene*). Long-chain branches strongly affect the processability of polyethylene and prevent the growth of polyethylene crystals on cooling. As a matter of fact, crystal growth is blocked by the presence of branch points in the main polyethylene chain, and only slightly affected by the length of the branches (by their molecular weight). By contrast, processability is strongly affected by the presence of long-chain branches and almost unaffected by short-chain branching. Since amorphous polyethylene has lower density than fully crystallised polyethylene, and since crystallisation of polyethylene is fast, density provides a direct measure of the crystallinity (the volume fraction of crystalline material). Therefore, *HDPE* is constituted by linear polyethylene chains with a reduced amount of long-chain branches (less than 6 branch points per 1000 C atoms). Conversely, *LDPE* is constituted by chains with a significant amount of

Table 10.7 Mechanical properties of polymers

Abbreviation	Material	Density (kg m^{-3})	Tensile modulus (GPa)	Tensile strength (MPa)	Elongation at rupture (%)	Impact resistance (w/slot) (kJ/m^2)
PVC	Polyvinyl chloride	1,300–1,500	1.0–3.5	30–70	10–300	2–50
PU	Polyurethane	1,140–1,260	–	–	–	–
PE	Polyethylene	914–960	0.2–1.4	8–35	100–1,200	30–100
PS	Polystyrene	1,040–1,060	2.0–3.3	45–65	1.0–3.0	2
PP	Polypropylene	900–910	1.0–1.6	25–40	100–1,000	3–17
UP	Unsaturated polyester	1,100–1,480	2.0–4.5	30–70	0.6–1.7	4
PC	Polycarbonate	1,100–1,250	2.0–3.0	56–66	100–130	20–30
PMMA	Polymethyl methacrylate	1,170–1,200	2.7–3.2	50–80	2–8	2
POM	Polyacetal	1,410–1,420	2.8–3.6	60–70	25–75	8
ABS	Acrylonitrile-butadiene-styrene copolymer	1,020–1,060	1.5–3.5	30–60	15–30	7.0–20
PA 6	Polyamide 6 (nylon 6)	1,130–1,150	2.0–2.8	65–86	60–300	15–20
MF	Melamine formaldehyde	1,400–1,570	5.0–9.0	30–60	0.6–0.8	2
PET	Polyethylene terephthalate	1,350–1,370	2.4–3.1	50–60	50–300	4
PBT	Polybutylene terephthalate	1,300–1,320	2.0–2.3	40–59	150	4
PPO	Poly(*p*-phenylene oxide)	1,060–1,100	2.0–2.5	45–75	50–70	12
CA	Cellulose acetate	1,280–1,300	2.1–2.9	19–55	3–30	15
CAB	Cellulose acetate butyrate	1,150–1,220	1.4–1.8	14–45	4–40	30
PA 12	Polyamide 12	1,010–1,020	1.6–1.7	55–65	250–300	10–20
PPS	Poly(*p*-phenylene sulphide)	1,300–1,500	3.4–4.1	70–125	1.6–3.0	1–2
PES	Poly(ethersulphone)	1,270–1,370	2.4–2.9	70–85	30–80	6–10
PSU	Poly(sulphone)	1,240	2.4–2.8	70–100	25–80	3–4
PTFE	Poly(tetrafluoroethylene)	2,100–2,200	0.3–0.6	20–35	350–550	13–15
PI	Poly(imides)	1,330–1,430	3.3–6.0	75–120	1.0–8.0	1.5–3.0
PEEK	Poly(ether-ether-ketone)	1,170–1,250	0.1–0.3	25–44	350–700	100

(continued)

Table 10.7 (continued)

Abbreviation	Material	Density (kg m^{-3})	Tensile modulus (GPa)	Tensile strength (MPa)	Elongation at rupture (%)	Impact resistance (w/slot) (kJ/m^2)
EVA	Ethylene vinyl acetate	920–950	0.1	10–20	600–900	>100
PS-i	High-impact PS	1,040–1,060	2.0–2.8	26–38	25–60	5–13
SAN	Styrene-acrylonitrile	1,060–1,080	3.2–3.6	65–85	2.0–5.0	2–3
PF	Phenol formaldehyde	1,300–1,400	6.0–12	30–50	0.4–0.8	2
UF	Urea-formaldehyde	1,470–1,520	70–100	30–60	0.5–10	2
	Epoxy resins	1,110–1,400	2.2–40	30–70	1–10	3
	Ionomers	940–960	0.2	28–35	250–500	40–50

Table 10.8 Thermal properties of polymers

Abbreviation	Distortion temperature (°C)	Linear expansion coefficient (°C × 10^{-5})	Thermal conductivity (W × m^{-2-1} K^{-1})	Critical oxygen index	Water absorption (24 h) (%)	Price (€/kg)
PVC	60–80	5–10	0.12–0.22	0.47	0.04–0.4	0.36
PE	30–55	13–25	0.25–0.6	0.17	<0.01	0.64
PS	80–100	6–10	0.12–0.17	0.18	0.03–0.1	0.52
PP	45–60	8–15	0.16–0.24	0.17	0.02	0.4
UP	230	10–18	0.2–0.7	0.3–0.5	0.05–0.5	1.76
PC	130–145	4–7	0.14–0.2	0.25–0.34	0.16	2.2
PMMA	65–100	6–17	0.13–0.2	0.17	0.1–0.4	1.32
POM	110–125	8–14	0.15–0.2	0.16	0.2–0.25	1.68
ABS	80–120	8–12	0.13–0.3	0.19	0.2–0.8	1
PA 6.6	66–110	8–10	0.17–0.24	0.29	0.8–1.6	2.08
MF	130	5–6	0.5	–	0.1–0.6	1.12
PET	60–80	7–12	0.15–0.25	–	0.2–0.3	1.36
PBT	100–300	6–10	0.12–0.2	0.2–0.3	0.08	1.96
PPO	125–140	6–7	0.16–0.21	0.29	0.05–0.25	1.88
CA	60–90	6–10	0.15	0.25	2–6	2.2
CAB	62–70	6–10	0.14	0.19	1–3	2.2
PA 12	60–110	9–12	0.17–0.23	0.25	0.25	3.92
PPS	135–137	5.0–5.5	0.2–0.24	0.44	0.02–0.05	3.88
PES	203	5.5	0.13–0.18	0.34–0.38	0.2–0.3	8
PSU	174–180	5.5–5.6	0.19–0.27	0.31	0.02–0.2	5.28
PTFE	250–260	10–14	0.19–0.25	0.95	0.01	6.4
PI	240–360	3.4–6.5	0.6–0.65	0.36	0.3–0.6	17.6
PEEK	55–66	17–21	–	–	0.3–0.5	
EVA	35–60	16	0.35	–	0.05–0.15	0.6
PS-i	80–100	7–8	0.13–0.17	–	0.08–0.6	0.56

(continued)

Table 10.8 (continued)

Abbreviation	Distortion temperature (°C)	Linear expansion coefficient (°C × 10^{-5})	Thermal conductivity (W × m^{-2-1} K^{-1})	Critical oxygen index	Water absorption (24 h) (%)	Price (€/kg)
SAN	80–105	3–8	0.13–0.17	0.19	0.2–0.3	0.96
PF	150–190	3–5	0.35	0.4	0.3–1.2	0.72
UF	130	5–6	0.4	–	0.4–0.6	0.92
Epoxy resins	100–200	6–11	0.2–0.9	0.24	0.05–0.3	2.4
Ionomers	38–455	5–6	0.25	–	0.1–1.4	0.96

long branches (*branched polyethylene*). *LLDPE* is a short-branched low-density polyethylene: it combines the low crystallinity and other characteristics of LDPE and the improved processability of HDPE.

It is interesting to remark that in old books and papers, HDPE was known as "*low-pressure polyethylene*" and low-density polyethylene was known as "*high-pressure polyethylene*", according to the type of reactors used at that time. Nowadays, it is possible to produce low-density polyethylene at low pressure, so the old nomenclature is meaningless and must be avoided.

Low-density (branched) polyethylene (0.910–0.935 g/cm^3) is a flexible material with remarkable toughness even at low temperatures (impact resistant), good resistance to chemical agents, low water vapour permeability, good electrical insulator, good transparency and easy processing. It is mainly used as a film (agricultural film, packaging), and it is also used as sheath in cable extrusion.

In practice, LLDPE is produced by copolymerisation of ethylene with α-olefins: 1-butene, 1-hexene, 4-methyl-1-pentene, 1-octene, etc. The result is a (linear) polyethylene main chain, having a number of short-chain branches of 3–10 carbon atoms. The density of short-chain branches (or the number of branching points per unit length in the main chain) is directly proportional to the ratio of α-olefin/ethylene feeding the reactor. Since the density of short-chain branches is also directly related to crystallinity, the ratio of α-olefin/ethylene also controls the density of the final product. In conclusion, the properties of linear polyethylenes depend essentially on two variables: the chain length, related to the molecular weight, and the number of short-chain branches per unit length of the main chain, related to density.

By feeding the appropriate ratio α-olefin/ethylene, grades of LLDPE with very low degree of crystallinity can be obtained; the common designation for such grades is *flexomers*. Flexomers have density below 0.91 g/cm^3.

Ethylene can also be copolymerised with vinyl acetate, ethyl acrylate and acrylic acid. The resulting copolymers share the good chemical resistance of polyethylene to improved adhesion properties.

Ultra-high-molecular-weight polyethylene (UHMWPE) has a molecular weight of a few millions of dalton. UHMWPE is the known thermoplastic with higher fracture toughness. It combines very good resistance to abrasion (one order of magnitude higher than carbon steel) to a very low coefficient of friction, self-lubricity and superior chemical resistance, and it is bioinert. As a matter of fact, UHMWPE must be considered as a specialty engineering thermoplastic by both its properties and price. The applications of UHMWPE include articular prosthesis and armour.

The most important applications are mentioned in Tables 10.9, 10.10 and 10.11.

10.5.2 Polypropylene

Polypropylene is obtained by polymerising propylene gas [$CH_3CH{=}CH_2$], using the appropriate catalysts. Due to the asymmetry of the monomers, the spatial

Table 10.9 Branched polyethylene

Branched polyethylene (PE)
Low-density PE $[0.910 < \rho/(\mathrm{g\ cm^{-3}}) < 0.935]$
LDPE Shore hardness D44-50 (Roughness at low temperatures, resistance to impacts and chemical agents, flexibility, transparency, processability, low water vapour permeability, electrical insulation). Film (packaging, agricultural film), extrusion coating (wires and cables), food packaging, variety of utensils
LDPE copolymers
EVA (*ethylene-vinyl-acetate*) (flexibility, toughness, adhesion)
EEA (*ethylene-ethyl-acrylate)* (toughness, flexibility, film, pipe)
EMA (*ethylene-ethyl-acrylate)* (thermal stability, film, coextrusion)
EVOH (*ethylene-vinyl alcohol)* (gas barrier, packaging)
Cross-linked polyethylene (PEX)
PEX (heat resistant up to 150 °C; hot water pipes for residential use)

Table 10.10 Linear low-density polyethylene

Linear low-density polyethylene
Flexomers $[0.88 < \rho/(\mathrm{g.cm^{-3}}) < 0.910]$ copolymers with α-olefins
ULDPE (ultra low-density PE): *VLDPE* (very low-density PE)
(Resistance to environmental cracking, flexural fatigue, impact and penetration, toughness at low temperatures)
Film for packaging, injection-moulded parts
Linear low-density PE $[0.915 < \rho/(\mathrm{g.cm^{-3}}) < 0.940]$ copolymers with α-olefins
LLDPE (linear low-density PE): Shore D55-56
(Toughness at low temperatures, tensile strength, resistance to penetration, wear and impact)
Film for packaging, geo-membranes, pipe and sheet extrusion
Medium-density linear PE $[0.926 < \rho/(\mathrm{g.cm^{-3}}) < 0.940]$ copolymers with α-olefins MDPE

Table 10.11 High-molecular-weight linear polyethylene

High-molecular-weight linear polyethylene
High-density PE $[0.945 < \rho/(\mathrm{g\ cm^{-3}}) < 0.967]$
HDPE: Shore D66-73 (Toughness at low temperatures, tensile strength, resistance to environmental cracking, electrical insulation)
Liquid storage (tanks, drums), containers, pipes and extruded profiles, hospital material, geo-membranes
High-molecular-weight high-density PE $[2 \times 10^5 < \mathrm{M}/(\mathrm{g.mole^{-1}}) < 5 \times 10^5]$
HMW-HDPE $(0.944 < \rho/(\mathrm{g\ cm^{-3}}) < 0{,}954)$ (Tensile strength, resistance to environmental cracking, abrasion, chemical agents, toughness at low temperatures and low water vapour permeability)
Large diameter pipes, large-scale containers, ultrafine films
Ultra-high-molecular-weight PE $[3 \times 10^6 < \mathrm{M}/(\mathrm{g\ mole^{-1}}) < 6 \times 10^6]$
UHMWPE: Shore D61-63 (Excellent abrasion resistance (around 10 times higher than carbon steel), very good toughness at low temperatures, low coefficient of friction)
Manufacture or coating of parts that require toughness at low temperatures, self-lubrication and resistance to corrosion, high modulus fibres, components for corrosive liquid pumps, gears, medical implants

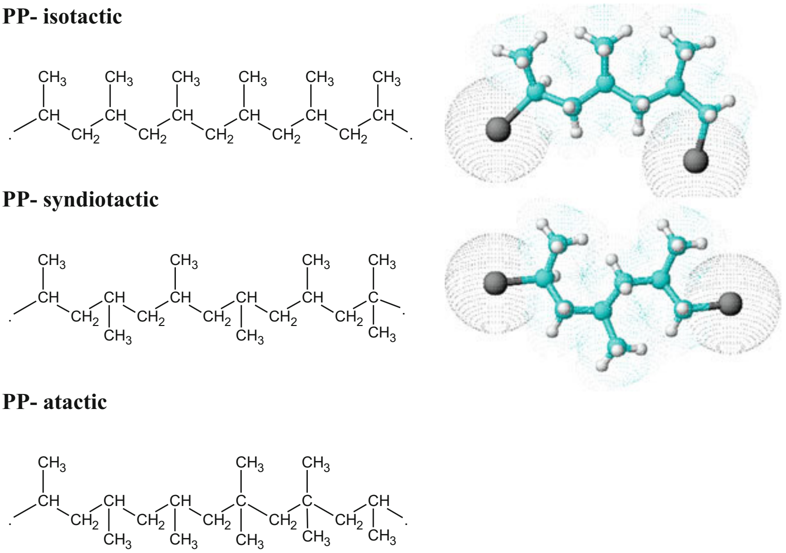


Fig. 10.2 Polypropylene isomers

insertion of methyl groups (–CH_3) in the chain can be carried out in several ways, depending on the type of catalyst chosen as well as the way the process is controlled, giving rise to one of three types (isomers) of polypropylene that have different physical and chemical properties: isotactic polypropylene, syndiotactic polypropylene and atactic polypropylene (see Fig. 10.2).

In *isotactic polypropylene* (i-PP), the methyl groups are arranged on the same side of the carbon chain. Isotactic polypropylene is a semicrystalline polymer that melts at around 165 °C and undergoes glass transition at 10 °C. Commercial industrially produced polypropylene is more than 90 % of that polypropylene.

In *syndiotactic polypropylene* (s-PP), the methyl groups are arranged alternately along the carbon chain. s-PP is a semicrystalline polymer that melts at around 125 °C and undergoes glass transition at −5 °C. Commercial use of s-PP was tiny until a very short time ago; industrial production of syndiotactic polypropylene began less than 15 years ago. Recently, the advantages of using s-PP produced with metallocene catalysts as insulation for electricity supply cables (600 V–22 kV) have been demonstrated.

In *atactic polypropylene* (a-PP), the methyl groups are arranged randomly along the carbon chain. a-PP is amorphous: it does not have a melting point and its glass transition temperature is −20 °C. A-PP is a by-product of industrial production of iso-polypropylene using Ziegler–Natta catalysts, and has little commercial interest. It is used in adhesives and caulking. The main industrial use of atactic polypropylene is as a modifier for bituminous binders used in waterproofing membranes. In Europe, waterproofing membranes using modified bitumen correspond to 65 % of the total market (data from 2006).

Polypropylene is highly resistant to chemical agents and solvents. The use of polypropylene includes the production of containers, electrical appliance frames, tubes and geo-membranes. Polypropylene and polypropylene copolymers are widely used in the automotive industry: bumpers, internal panels, etc. Isotactic polypropylene can also be extruded to fibres. Iso-PP fibres found large utilisation in bags, ropes, carpets and geotextiles.

10.5.3 Polyvinyl Chloride

PVC is obtained by polymerising vinyl chloride [CH_2CHCl] or VCM (= vinyl chloride monomer). VCM is a gas at normal pressure and temperature conditions; it is liquefied under pressure and then polymerised. The properties of PVC depend on the polymerisation techniques used: *suspension polymerisation, emulsion polymerisation, solution polymerisation* and *mass polymerisation*. In any case, the pure polymer obtained directly from the reactor is hard, brittle and cannot be processed immediately; prior to processing, it should be formulated. Formulation includes additives such as thermal stabilisers and co-stabilisers, plasticisers, impact modifiers, "external" (immiscible) lubricants, "internal" (miscible) lubricants, pigments, foaming agents (if needed), antioxidants, ultraviolet stabilisers, etc.

S-PVC ("*suspension*" PVC) is synthesised as follows. First, the water-insoluble VCM is emulsified ("suspended") in water as droplets: the emulsifiers ("suspending agents") are a combination of ionic surfactants, polyvinyl alcohol and others. Then, free water-insoluble radical initiators are fed. The initiators are soluble in the dispersed phase, so the polymerisation starts in the VCM droplets; as the reaction proceeds, the liquid droplets become beads ("pearls"): the final result is a water suspension of beads with diameters between 60 and 300 μm. Around 80 % of PVC in the market is produced by this way. It is worth noting that the term "*suspension polymerisation*" is inadequate. The polymerisation proceeds in an emulsion; the suspension is obtained when the polymerisation ends and polymer beads are formed.

E-PVC ("*emulsion*" PVC) is produced as follows. First, VCM is emulsified in water by surfactants, in the form of droplets; emulsifier molecules are also present as micelles (4–10 nm diameter) and each micelle may contain some VCM monomers. Here the polymerisation initiators are water soluble. Polymerisation starts in the micelles; some VCM molecules may migrate to micelles during polymerisation and be added to the growing chain. After some time, the micelles become latex particles (20–500 nm diameter). The polymerisation further continues in the latex particles: they are fed by the emulsified monomer droplets until no more droplets remain. The final result is a latex that, after partial drying, yields a paste with particle size between 15 and 25 μm. Again the term "*emulsion polymerisation*" is inadequate; polymerisation takes place in micelles and not in the emulsion droplets.

Dispersion PVC is composed of fine particles (10–20 μm) of PVC polymer or copolymerised with other vinyls, dispersed in a plastifying liquid to form a plastisol. By adding a volatile solvent to a plastisol, an organosol is obtained. Plastisols and organosols are produced from emulsion PVC, or microsuspension PVC. Dispersion PVC corresponds to around 10 % of the total produced.

Microsuspension PVC (PVC-MSP) is obtained through a variation of suspension polymerisation, with initiators that are soluble in monomers; the mixture is homogenised, which promotes dispersion and produces smaller particles.

PVC-M (*bulk* PVC) is polymerised in bulk, which means only in the presence of the monomer, without addition of solvents, non-solvents, emulsifiers, etc. (in practice, some solvent is used . . .). As the polymerisation proceeds, PVC precipitates since it is insoluble in VCM monomer. The particles obtained are around 150 μm in diameter. PVC-M corresponds to around 10 % of the total PVC produced.

The most important properties of PVC are superior fire retardancy, high ignition temperature (455 °C) and relatively low heat release in burning; moreover, it presents strong resistance to oxidation, good chemical resistance to acid and alkali chemicals.

The main markets for PVC are building and construction, packaging, the electrical and electronics industry (wire coating and cable coating for electrical applications, etc.). PVC has a wide variety of uses: producing synthetic leather, coatings for electrical wires and cables, rigid pipes for water and sewage, flexible tubes for water, window frames, geo-membranes, various types of packaging, cloths, shower curtains, etc. Foamed PVC is widely used in tubing.

10.5.4 Polystyrene

Polystyrene (PS) is a thermoplastic resin normally obtained by the radical polymerisation of styrene, initiated with benzoyl peroxide; the typical molecular weight values are in the order of 300 kg/mol. Polystyrene can be copolymerised with several monomers: butadiene, acrylonitrile, methyl methacrylate and acrylates.

The most characteristic properties of polystyrene are highly rigid, high refractive index ($n = 1.59$) and transparency, low resistance to organic solvents and environmental agents. Its most significant uses are manufacture of houseware and transparent rigid packaging.

Polystyrene can be used after being foamed. Polystyrene foam, also known as expanded polystyrene (EPS), is an excellent thermal insulator. It has a thermal conductivity of 0.03 $W\ K^{-1}\ m^{-1}$ and a density of 30 kg/m^3 (it can even reach 15 kg/m^3). EPS corresponds to around 10 % of the polymer market for construction. It is also frequently used in packaging, specifically the electrical and electronics industry.

10.5.5 Polyurethanes

Polyurethanes are produced by a reaction between two monomers: one polyol (polyalcohol) with several hydroxyl groups (–OH) (e.g. ethylene glycol) and a polyisocyanate, with several isocyanate groups (–N=C=O): for example, toluene

Table 10.12 Polyurethanes

Foams
Low-density foams (10–80 kg/m^3)
Flexible: pillows, vibration absorbers
Rigid: light panels with good structural rigidity and thermal insulation
High-density foams (> 100 kg/m^3)
Flexible
Self-forming shell: footwear
Microcellular elastomers: footwear (soles)
Rigid: structural uses
Thermoplastic elastomers: abrasion resistance, good resistance to oils and non-polar solvents
Adhesives, glues and sealants: adhesives for flexible materials, for rubbers, for metal-metal adhesion, for metal-rubber adhesion, and for metal-plastic adhesion
Paints, lacquers and cellular coatings: good resistance to wear and very good toughness

diisocyanate (TDI) and methylene diphenyl diisocyanate (MDI). Depending on the monomers selected, one may get rigid polyurethanes, polyurethane elastomers including thermoplastic elastomers, and several types of foams and gums can be synthesised.

The main consumers are in the automotive, transport, construction and furniture industries.

One of the great advantages of polyurethanes as a class of materials is their *versatility*.

- *Versatility in formulation*: By choosing the appropriate chemical groups to which the hydroxyl and isocyanate are bonded, it is possible to synthesize linear chains, chains with controlled branching, totally or partially crosslinked chains, chains constituted by *segments* with variable flexibility (rigid, flexible). The final product can vary between ultra-flexible elastomer and ultra-rigid thermosetting material.
- *Versatility in density*: Depending on the conditions under which polymerisation takes place, a foam with controllable characteristics can be formed. Therefore, the density of these materials can vary between 6 and 1,220 kg/m^3.
- *Versatility in processing*: It is possible to control the nature and properties of the final product by carrying out simultaneously polymerisation and processing (*reactive processing*).

Table 10.12 shows the different characteristics of polyurethanes.

10.5.6 Elastomers

Elastomers are “ideal” materials that present mechanical properties and behaviour similar to the ones of vulcanised natural rubber. Real materials only behave as elastomers within a given temperature range, so by classifying one given material as an elastomer, it must be understood that the material behaves like an elastomer in some temperature range. Vulcanised rubber behaves like an elastomer at room temperature, but it no longer behaves like an elastomer at –50 °C: at that temperature, vulcanised rubber behaves like a glassy polymer. The space shuttle accident on 28 January 1986 was caused by the fact that the silicone used for a specific seal (sealing O-ring) did not present the expected elastomer behaviour at the temperature at which the launch was done (below 0 °C).

The following characteristics are associated to elastomer behaviour:

- *Flexibility*: Young's modulus and shear modulus are in the range of 10^5–10^7 Pa.
- *Deformability*: when stretched, a band should be able to withstand a large strain without rupture (more than 200 %, which means more than three times the initial length).
- *Elastic recovery*: after stretching is released, the band should recover soon the initial shape and dimensions.

In practice, these characteristics are achieved through cross-linking of linear polymer chains. In molten polymers, monomers experience thermal agitation and are free to diffuse as well as polymer chains. Diffusion of polymer chains as a whole in the melt is rather slow: the diffusion coefficient is inversely proportional to the square of the number of monomers in the chain. Polymer chains bound to a polymer network in more than two points cannot diffuse as a whole anymore; only fluctuations around some fixed position are allowed. On the other hand, chemical cross-linking will only affect the monomer mobility for the monomers directly involved in the cross-link. Since only few monomers are directly involved in cross-links, for most of the monomers belonging to cross-linked chains, local diffusion due to thermal agitation is not affected. Therefore monomers "feel" equally free to fluctuate both in free chains and in cross-linked chains, due to thermal agitation. In other words, monomers keep liquid-like mobility in a cross-linked rubber. The rubber does not flow because the chains (the centres of mass of every chain) are immobilised by the cross-links.

The amount of cross-linking should fall within the following limits:

- The cross-link density must be weak enough to allow that glass relaxation (or glass "transition") remains detectable by usual ways; otherwise, a thermoset material has to be formed instead of an elastomer.
- The cross-link density must be sufficiently strong so that the material becomes a viscoelastic solid: the equilibrium modulus must be finite, greater than zero. It is thereby distinct from a partially cross-linked viscous liquid, which can flow more or less easily.

Chemical cross-linking may be effective through chemical reactions, which is the most common scenario. Chemical cross-links are irreversible and cannot be eliminated by heating without severe degradation of the polymer chains.

Physical cross-linking results from physical interactions of attractive nature, the neat effect of which is to immobilise some of the chain monomers. For instance, the adhesion of few chain monomers to the surface of fillers may block the diffusion of the whole chains in a way very similar to the one of chemical cross-links. Segregation may also be a cause of physical cross-linking. For instance, let us consider a di-block copolymer S-B and let us suppose that segregation of the S blocks leads to formation of a number of solid nodules of S distributed in the bulk, in a way similar to fillers. Above the glass temperature of B (−60 °C, if B is polybutadiene) and below the glass temperature of S (100 °C if S is polystyrene), the block copolymer behaves like an elastomer: the glassy nodules of S immobilise the B chains like fillers. In this case, the nodules of S perform as *active fillers* since they are chemically bound to the B sub-chains.

Physical cross-linking is reversible. Physical adhesion between of polymer chains and one filler can be reversed by use of an appropriate solvent. Physical segregation in block copolymers can be eliminated by heating up to a temperature above the glass transition of all the blocks present; the nodules are molten and no more behave as active fillers.

Physically cross-linked block copolymers are called *thermoplastic elastomers* since they behave like elastomers in one given temperature domain, and can be processed as thermoplastics at higher temperatures.

10.5.6.1 Thermoplastic Elastomers

Commercially, the following classes of thermoplastic elastomers are generally considered (by increasing order of price and performance):

- *Styrenic thermoplastic elastomers* (TPE-S)—formed of block, linear or branched styrene copolymers [SBS (styrene-butadiene-styrene), SIS (styrene-isoprene-styrene), SEBS (styrene-ethylene-butylene-styrene) and SEPS (styrene-ethylene-propylene-styrene)]
- *Olefinic thermoplastic elastomers* (TPE-O) or *thermoplastic polyolefins* (TPO)—blends of PP, EPDM or EP rubber, PE, fillers and additives
- *Alloys of thermoplastic elastomers*:
  - *Thermoplastic vulcanised rubber* (TPE-V or TPV)—bicomponent mixture of rubber and plastic, (ethylene-propylene elastomer or nitrile rubber and PP). Rubber and thermoplastic are first mixed and then vulcanised in an extruder; the crosslinking of the blend morphology obtained after intensive mixing is called *dynamic vulcanisation*.
  - (XTPL)—dynamic vulcanisate blends in which ethylene interpolymers replace rubber at the flexible phase
  - MPR (*melt processable rubber*)—blends of random copolymers of ethylene and olefins or chlorinated olefins (“ethylene interpolymer”) crosslinked *in situ*
- *Thermoplastic polyurethanes* (TPE-U or TPU)—block copolymers formed of alternately rigid and flexible segments; the polyol is either a polyester polyol or a polyether polyol. Esters are generally tougher but hydrolyse and degrade in the

presence of water; ethers do not hydrolyse or biodegrade. They show improved mechanical properties and high wear resistance.
- *Polyester-ester thermoplastic elastomers* (TPE-E) are dynamic vulcanisates combining polyester rubbers and polyester thermoplastics.
- *Thermoplastic polyamides* (TPE-A) are dynamic vulcanisates of polyamides and elastomer block copolymers

Building and household applications represent more than 30% of the market for applications of dynamic vulcanisate thermoplastic elastomers.

10.6 Polymer Testing

Materials characterisation and testing is the standard way of assessing and quantifying their properties and performance. In general, a set of reference tests are mandatory for a product to be sold and get acceptation by the market. The chosen tests depend on the intended applications. In particular, the usefulness of polymer testing stands on multiple purposes:

1. *Quality control*: It is a way of evaluating that some required set of properties fits to given specifications. Quality control tests are standard for checking the output of one production line; they are by their nature short-term tests ("everyday tests"). Quality control tests are also standard for acceptation of raw materials and for certification.
2. *Design purposes*: Components design and parts design currently require a set of data values about material constants and material functions which can only be provided by the appropriate set of tests.
3. *Materials selection*: The requirements for any part or component involve, in general, shape and performance. The selection of the best material to fulfil those conditions stands on the prior knowledge of a set of material constants and material functions of the candidate materials. Polymer testing enables comparison of different material properties and helps selecting the most appropriate ones.
4. *Long-term performance*: Performance involves two different and complementary aspects: short-term performance and long-term performance. Short-term performance is assessed by quality control tests. Long-term performance involves both a combination of specific tests and further analysis and extrapolation beyond the collected data. For instance, the expected lifetime of domestic hot water plastic pipes must be, at least, 50 years; of course, nobody is waiting 50 or more years for the results of the test … . Creep, physical ageing and weathering are examples of long-term performance tests that stand on this kind of extrapolation procedures.
5. *Development and optimisation of materials*: Polymer testing makes it possible to optimise compositions and formulations for both current and new applications. Development and optimisation are not only focused on final properties.

For instance, processing aids and processing conditions can also give rise to substantial changes both in costs and final properties of the output products.

6. *Model validation*: There is nothing more practical than a good theory! Therefore, materials testing and, in particular, polymer testing, is the best way to validate or contradict theoretical predictions and models.

Material properties can be split in two main broad domains: "stiffness" properties, related to constitutive equations and "strength" properties related to "resistance" to external actions.

The first one involves *constitutive properties* of the material itself. They include *material constants* such as Young's modulus or shear modulus, *material functions* describing creep and stress relaxation. The second one involves the evaluation of how much the material resists to external agents, keeping the integrity of the parts (or components) and maintaining the performance within acceptable limits. Examples are impact strength, fatigue strength, resistance to solar radiation, ageing by environmental agents, etc.

It is desirable to distinguish among different levels of properties to be tested:

1. *Material properties*: Density and Young's modulus (E), for example, are properties (material functions) of one given material. They must not depend on geometric shape. Since tests are performed on specimens with some given shape, some care has to be taken to ensure that no confusion between specimen properties and material properties is made.
2. *Specimen properties*: Young's modulus (E) is currently computed from the measurement of the rigidity ($E \times I$) of a specimen with a given geometric shape; here I is the moment of inertia of cross-sectional area and only depends on the geometric shape of the specimen. Errors in the evaluation of specimen geometry (on I) propagate to the evaluation of the material constant E. Such errors can be reduced by improving the accuracy of the measurements and by increasing the number of specimens tested.
3. *Sample properties*: The *exact* determination of the fracture energy of 10^5 shields can only be done if all shields are destroyed: it is useless. More useful is the *estimated* fracture energy of 10^5 shields (the *statistical population*) from data collected from tests performed on a (statistical) *sample* of a few shields taken from that population. Elongation at break is another example of a property which stands on the results of tests performed on a collected sample and extrapolated to the corresponding statistical population.
4. *Individual specimen properties*: Fracture energy is characteristic of one single rupture process that occurred in a given individual specimen. It can be accurately measured once, in an instrumented impact tester; it cannot be repeated. As a matter of fact, crack propagation is a sequence of a great number of correlated elementary steps, with a strong dependence of the initial conditions: its dynamics brings similarities to chaotic systems. Therefore, even if it were possible to get a set of exact replica specimens, cracks should not be the same so experimental results would also not be the same.

5. *Statistical population properties*: There are some properties of a statistical population that can be estimated from data provided by a sample of that population. Single properties such as the mean inner diameter of a population of plastic pipes can be correctly estimated by standard statistical procedures. The "inner diameter" is a single property that has the same meaning when dealing with one specimen, one sample or the full population; it is also a *test-independent property*, since its value does not depend on the kind of instrument used to measure it. But there are other properties conotated to "strength" such as impact strength, fatigue strength, among others, which are meaningful when associated to a statistical population and are meaningless when associated to just one specimen or even to one sample, because they are *test-dependent properties*. The measurement of the "inner diameter" is a single process, and the main errors involve the instrument and the operator. On the other hand, rupture by impact is the result of a complex sequence of correlated processes, from which a few global values (energy for crack iniciation, energy for crack propagation) are extracted. Since that sequence of correlated processes is expected to depend on the type of test chosen, the final result shall be test-dependent. This is the main reason why, the results of pendulum impact tests performed in the Charpy configuration or in the Izod configuration present no correlation. Such differences among different impact tests and geometries are enhanced when dealing with polymer materials. The same drawbacks apply, *mutatis mutandis*, on other "strength" properties like fatigue strength, environmental stress resistance and so on.

The mechanical and rheological properties of polymers must provide an appropriate description of the viscoelastic behaviour of these materials. The viscoelastic behaviour of materials is described by constitutive equations. The particularisation of a constitutive equation to a given material is done by taking the needed material constants or material functions. The elastic behaviour of a Hookean elastic solid is described by a constitutive equation: Hooke's law. The particularisation of this constitutive equation to a given material needs the knowledge of *material constants* such as Young's modulus E, the shear modulus G or the Lamé's constants of that material. The flow behaviour of a Newtonian liquid is described by Newton's law, or Newton's constitutive equation. The particularisation of that equation to a given fluid needs the value of a *material constant*: the shear viscosity.

For viscoelastic material like most polymers, "material constants" become time-dependent or frequency-dependent, and they are no more constants; they are replaced by *material functions* that include the time or the frequency dependence, and even the stimuli (stress or strain) dependence for non-linear materials.

For polymers, materials functions, in general, present a strong dependence of time. It is helpful to distinguish between *short-term properties* (hours, days) and *long-term properties* (years, the part's lifetime). Short-term properties are regularly checked in quality tests; they are deeply involved in *quality control* or in *short-term performance*. Long-term properties are directly related to *long-term performance*. Most often, assessment of long-term performance involves additional extrapolation

Table 10.13 Mechanical tests

	"Stiffness" properties	"Strength" properties
Short term	Elastic moduli E, G	Impact strength
	Poisson's ratio v	Tear resistance
		Yield stress
Long term	Stress relaxation	Dynamic fatigue strength
	Creep	Static fatigue strength (creep rupture)
	Elastic recovery	Weathering

procedures as in "accelerated" tests, where the intensity of stimuli is exacerbated to simulate a longer testing time. For example, in accelerated ageing tests, ultraviolet irradiation intensity is increased to simulate a longer period of irradiation. In fatigue strength both the amplitude of stress and the frequency may be increased to simulate extended testing time. Both methods are not rigorously equivalent, and some care with analysis of data is advisable (Table 10.13).

A typical set of current tests for thermoplastics is shown in the following table (Table 10.14).

Some tests will after be described and commented. Due to space limitations, the chosen tests were those which are more specific to polymers and which provide data values quite different from the ones found in other better-known materials, such as ceramics and metals. Some foam tests were considered because of their increasing use in building and construction. Polymer matrix composites were almost excluded in spite of their importance, because they are popular materials whose properties are easily available. For new materials, it is important to mention the so-called polymer concretes in which the binder is a thermoplastic or thermosetting resin.

10.6.1 Physical Tests

Physical properties include mechanical, thermal, electrical and optical properties. Standard methods of measurement are issued by a number of national or international organisations. The most important are International Organization for Standardization (ISO), American Standards for Testing and Materials (ASTM), British Standards (BS), Deutsche Institut für Normung (DIN) in Germany, Association Française de Normalisation (AFNOR) in France and Instituto Português da Qualidade (IPQ) in Portugal.

10.6.1.1 Sample/Specimen Preparation

It is very common to keep parts or specimens at rest for some time, after being produced. Relaxation of internal stresses inherent to processing may take days or even weeks. For thermosetting materials, post-cure continues for hours or a few days after manufacture.

Physical properties may vary with moisture content, and the specimens should be kept in a standard atmosphere beforehand. Standard ISO 295 specifies the

Table 10.14 Current tests for thermoplastics

Tensile geometry		
	Young’s (tensile) modulus	
	Tensile strength	
	Elongation at rupture	
	Yield strength	
Compression geometry		
	Compressive modulus	
	Compressive strength	
		Rupture
		Yield
Bend geometry		
	Flexural test	
	Flexural strength	
		Rupture
		Yield
Impact test		
	Impact resistance (IZOD)	
Hardness		
	Rockwell	
	Shore	
Thermal properties		
	Linear expansion coefficient	
	Heat deflection temperature under load	
	Thermal conductivity	
Density		
Water absorption		
	absorption after 24 hours	
	Absorption at saturation	
Dielectric rigidity		

following conditions for the standard atmosphere: temperature at 23 °C, relative humidity at 50 ± 5 % and air pressure between 86 and 106 kPa. The conditioning period can vary between 12 and 88 h, depending on the test; for most cases a conditioning period of 16 h before the test is enough. Standard ASTM 3574 recommends conditioning flexible foams for 12 h at 23 °C and at 50 ± 5 % relative humidity (RH) before the test. Generally, physical tests are carried out under conditions identical to those used to condition specimens.

10.6.1.2 Mechanical Properties

Mechanical properties are found by measuring the response to mechanical stimuli: either the stimulus is strain and the response is stress, or the stimulus is stress and the response is strain; polymers have a marked viscoelastic behaviour, linear or non-linear, depending on the amplitude of the stimulus. The material functions relevant for stress relaxation (relaxation modulus), creep (creep compliance) and hysteresis are extremely dependent on time and temperature. Caution should be taken when testing polymeric materials with tests designed for other types of materials that do not have such accentuated viscoelastic behaviour.

Elastic Properties

In a tensile test carried out in quasi-static conditions (at low crosshead speed), the specimen is stretched at constant crosshead speed until fracture (ASTM D412). Most of the characteristic parameters of a tensile test are defined in terms of the so-called “engineering stress” (force per unit original cross sectional area) and “engineering strain” (elongation per unit original length, l_0). At very low (infinitesimal) strain, there is no significant difference between the “engineering stress” and the Cauchy stress or “true stress” which is given by force per unit actual cross sectional area. Metals, ceramics, glassy polymers, and thermosets, present a low value elongation at break, so the error in using “engineering data” instead of “true data” is almost negligible. For materials able to hold up large strains without breaking, as it is the case of elastomers, flexible foams, thermoplastics presenting “cold drawing”, and so on, “engineering stress” can differ from “true stress” by a factor of 5, 10 or even more. The same holds for strain: Hencky strain or “true strain” [$\ln(l/l_0)$] and “engineering strain” values are quite different. For an extension ratio (l/l_0) equal to 10, the “engineering strain” is 9 and the Hencky strain or “true strain” is 2.3.

Therefore quantities such as the yield stress, the ultimate tensile strength (maximum value of “engineering stress”), the fracture stress (“engineering stress” at fracture) and the corresponding “engineering strain” values are of little help for characterisation of elastomers, flexible foams or ductile thermoplastics.

Elastomers are non-linear. To account for non-linear elastic behaviour, “moduli” at 100 , 200 and 300 % strain are taken. As pointed before, care has to be taken with the definition of strain for large strains. Very small strains are described by a unique measure, the infinitesimal strain; moreover, infinitesimal strains are additive. On the contrary, finite strains are non-additive, and several measures of strain may be considered. Since the elastic energy does not depend on the particular measure of strain chosen, for finite strains the value of the stress depends on the chosen measure of strain.

The tensile test for foams is described in standards DIN 53430 (rigid foams) and DIN 53571 (flexible foams).

Figures 10.3 and 10.4 display the results of a tensile test in natural rubber (Fig. 10.3) and in a high performance nitrile rubber (Fig. 10.4). Notice that natural rubber can be extended up to seven times the initial length and the nitrile rubber shown can be extended up to 13 times the initial length.

Tear Resistance

Tear resistance is currently measured in flexible foams (ASTM D3574), plastic films and sheets (ASTM D882) and elastomers (ASTM D624). Tests are carried out in notched specimens (Fig. 10.5) in order to create a strong concentration of stress

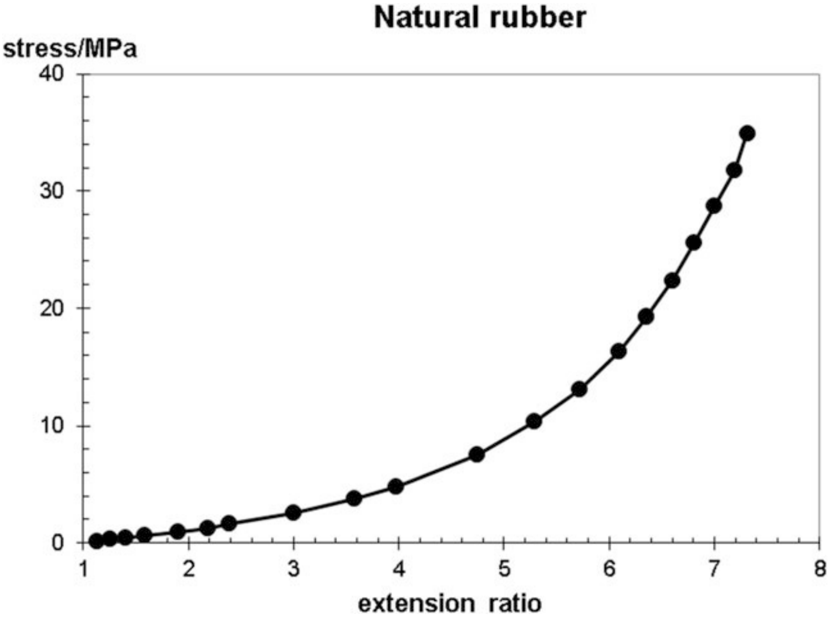


Fig. 10.3 Stress versus extension ratio for natural rubber (the maximum extension ratio is about 7.6)

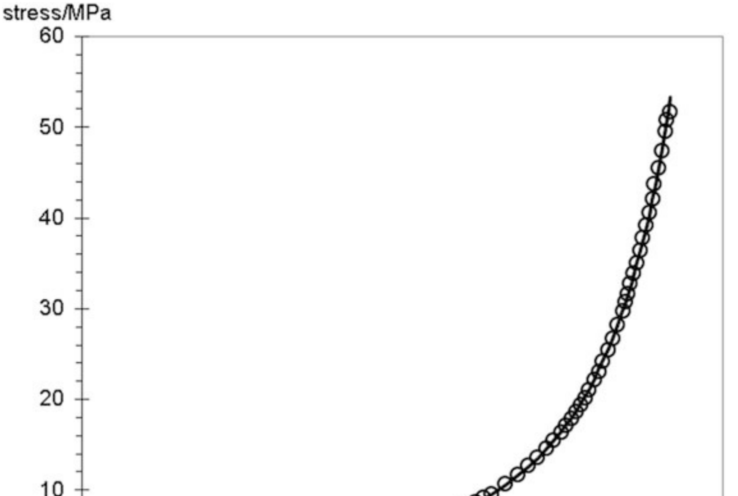


Fig. 10.4 Stress versus extension ratio for a special formulation of nitrile rubber (the maximum extension ratio is about 13). *Open circles*: experimental data. *Full curve* represents a fit of the Edwards–Vilgis theory to the experimental data

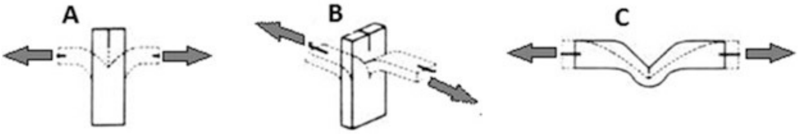


Fig. 10.5 Tear resistance in different geometries. (**a**) ASTM D3574 Foam tear strength. (**b**) ASTM D470 “trousers” geometry (for tear propagation). (**c**) ASTM D624 Die C test (for tear initiation)

close to the notch tip. The test method employs a constant rate of separation of the grips holding the specimen. The peak force is taken as the measure of the resistance to tear.

Resilience and Toughness

Resilience is the ability of the material to absorb elastic energy when it is elastically deformed by a given load and to release that energy upon unloading. In brittle materials, resilience is measured by the elastic deformation energy per unit volume absorbed up to the elastic limit. In elastomers and flexible foams, resilience is measured in a bouncing test: a sphere of steel is allowed to fall from height h, bounces on the elastomer and reaches height $h' < h$; the energy transferred by the sphere to the elastomer is proportional to h; the energy released by the elastomer to the sphere is proportional to h′. The h'/h quotient, given as a percentage, measures resilience (ASTM D3574) (Fig. 10.6).

Toughness is the ability of a material specimen to absorb energy until rupture. It is measured by the area under the stress-strain curve.

Compressive Strength

Compression tests measure the force necessary to compress or break a specimen placed between two parallel plates that are brought together at constant speed.

Rigid foams—The compressive strength of rigid cellular materials (ASTM D1621) is expressed as the compressive stress that causes a 10 % strain, or the compressive stress that causes rupture if it occurs at smaller strains (Fig. 10.7). For these tests, the shape and size of the specimen are important, as well as the parallelism of the surfaces touching the plates.

Flexible solids—In solids, the compressive stress is measured by the compressive force per unit cross section at a given compression ratio (ASTM D575).

Flexible cellular materials—During compression of a flexible foam, the stress versus strain curve displays three regimes. First, a linear regime is found, which corresponds to the starting of cell walls bending. Once buckling of the walls starts, the stress-strain curve shows a plateau that remains until most of the cell walls collapse by buckling. The third regime corresponds to the smashing of the buckled cell walls, and the stress starts increasing again. During unloading, the specimen returns to its original dimensions.

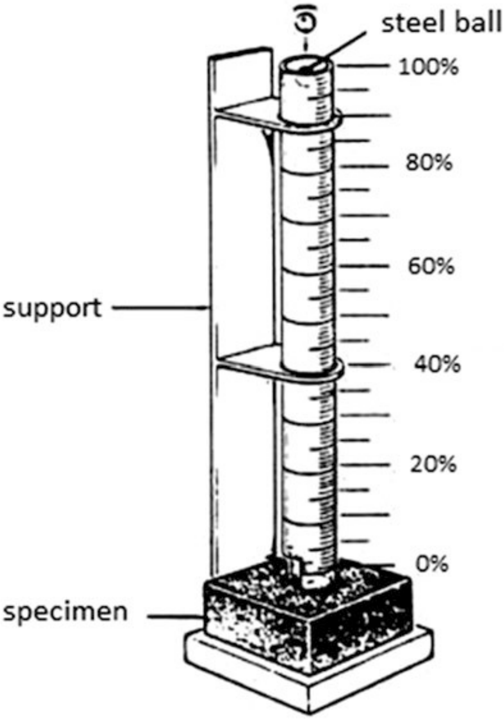


Fig. 10.6 "Rebound test" for determination of resilience in flexible foams and elastomers (ASTM D 3574)

Quite often, the loading and unloading curves do not coincide, and hysteresis occurs. The area of the hysteresis loop measures the energy dissipated during the hysteresis cycle (ASTM D2231, ISO 3386). The shape of the hysteresis loop depends both on cell geometry and on the material constituting the cell walls (Fig. 10.8).

Compression and Indentation

In polyurethane (PUR) flexible foams, the results of penetration tests by puncturing (lat. *punctio*, *-onis* = puncture) are sometimes confused with those for compressive strength (ISO 2439, ASTM D3574). The *indentation force deflection* is a load bearing test where it is measured the force per unit area needed to imprint a cavity in the foam with a given depth (25, 50 and 65 %) for a hole measuring 20 cm in diameter. For flexible foams, the comfort value is defined as the ratio between the indentation forces at 65 and 25 %. In the compressive strength test, the sample is compressed to 50 % of its original size for 60 s and the final load is measured.

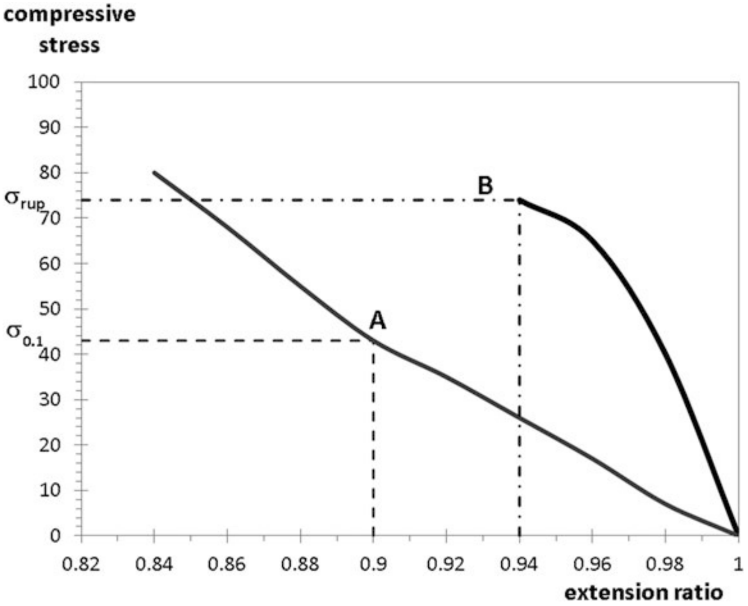


Fig. 10.7 Characteristic stress versus strain curves for a rigid cellular material. Compressive strength is the compressive stress $\sigma_{0.1}$ at 10 % strain (point A, *grey curve*). If there is rupture before, the compressive strength σ_{rup} is equal to the rupture stress (point B, *black curve*)

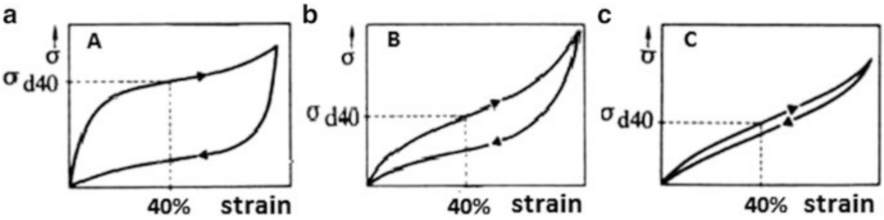


Fig. 10.8 Stress/strain curves of flexible foams. (**a**) High hysteresis. (**b**) Medium hysteresis. (**c**) Low hysteresis

Hardness

Hardness measures resistance to scratch. The hardness of solid materials is measured on arbitrary scales described in the methods of ASTM D785 and ASTM D2240. To establish the hardness properties of plastics, elastomers and foams, the Shore hardness test is normally used (Fig. 10.9). In this test, the penetration depth of a punch to which a well-defined load has been applied is measured 3 s after the load is applied. The result is shown as a number between 0 and 100, and by a letter (A or D), which specified the type of load; the A Shore scale is used for softer materials and the D Shore scale used for harder ones.

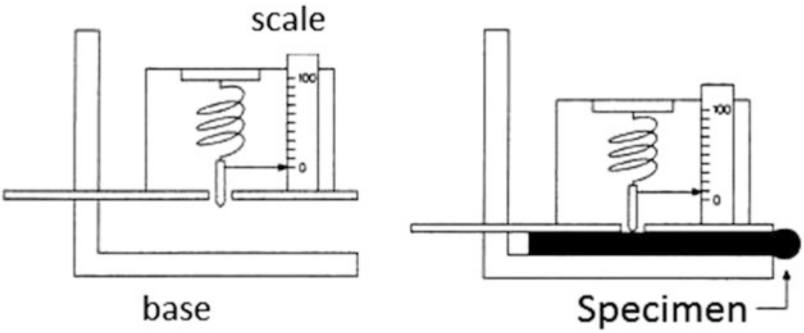


Fig. 10.9 Shore hardness test

Friction resistance

Resistance to friction or to slipping is an important property for materials. The friction forces oppose slipping and depend on the finish of the surface. It can be represented by the coefficient of friction, which is the ratio between the frictional force and the normal load applied to the sliding specimen (ASTM D1894 and D3028). In solid PUs with high hardness, low coefficients of friction are obtained.

Shear Strength

Shear strength is an important characteristic of rigid foams in sandwich-type structures. According to ISO 1922, the material is trapped between two flat parallel metal plates; shear is created by pulling the plates in opposite directions (Fig. 10.10).

Flexural Strength

Flexural strength shows the maximum stress that can be supported by a bar under flexion without rupture. This test is applied to rigid materials.

In the ISO 1209 flex test, a bar of rigid foam with standard dimensions is supported at the ends and in the centre (Fig. 10.11). During the test, the supports at the ends are moved at a rate of 10 ± 2 mm per minute, and the corresponding force at a deflection of 20 ± 2 mm is recorded. If the specimen breaks before a 20 mm deflection, the deflection force at rupture is recorded.

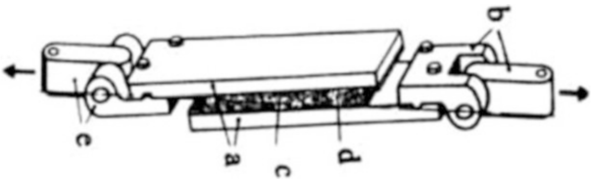


Fig. 10.10 Shear strength cell

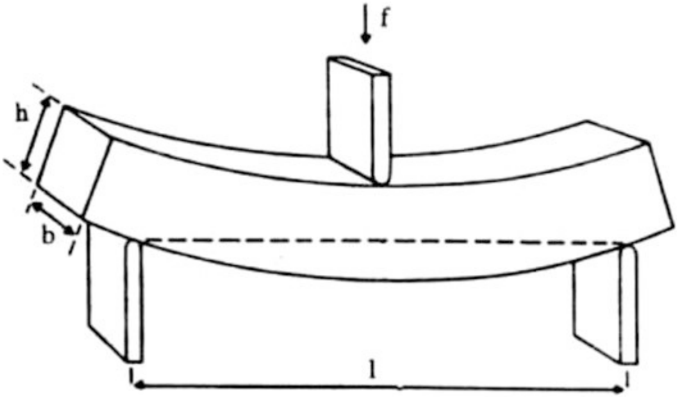


Fig. 10.11 Three-point flexural test

Impact Tests

There are several types of impact tests. The most commonly used involve a falling weight (ASTM D3029) or impact with a pendulum: the Izod test (ISO R180) and the Charpy test (ISO R179).

10.6.1.3 Endurance Evaluation

Endurance tests are designed to evaluate the long time performance of materials or parts. They include creep, permanent deformation, dynamic fatigue, weathering accelerated ageing, abrasion, etc.

Creep Tests

Creep tests consist of measuring the time evolution of the strain resulting from the application of a constant load. At small loads, linear viscoelastic behaviour is observed. For loads above some relatively low threshold, non-linear viscoelastic behaviour starts and its description and evaluation become more difficult.

In a creep test, the relevant material function is the creep compliance $J(t)$, defined by

$$\gamma(t) = J(t, \sigma_0)\sigma_0$$

where σ_0 is the (constant) stress applied and $\gamma(t)$ the strain. The reciprocal of the creep compliance is called the creep modulus (Fig. 10.12).

For non-linear materials, the creep compliance is both time dependent and stress dependent. The results of non-linear creep tests can be presented in several ways:

1. *Isobaric curves* (at constant stress) where the strain is plotted versus time, at constant stress. By changing the values of the stress, different isobaric curves are produced. In Fig. 10.13, creep data on polyamide 6,6 (PA66) is presented as isobaric plots.

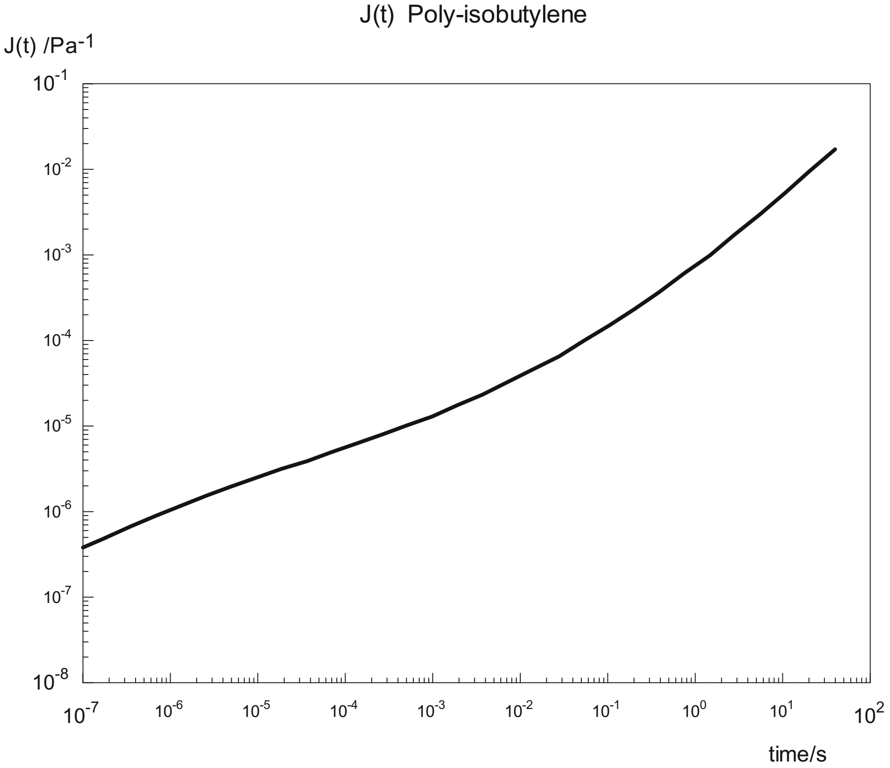


Fig. 10.12 Creep compliance $J(t)$ for a general thermoplastic (polyisobutylene)

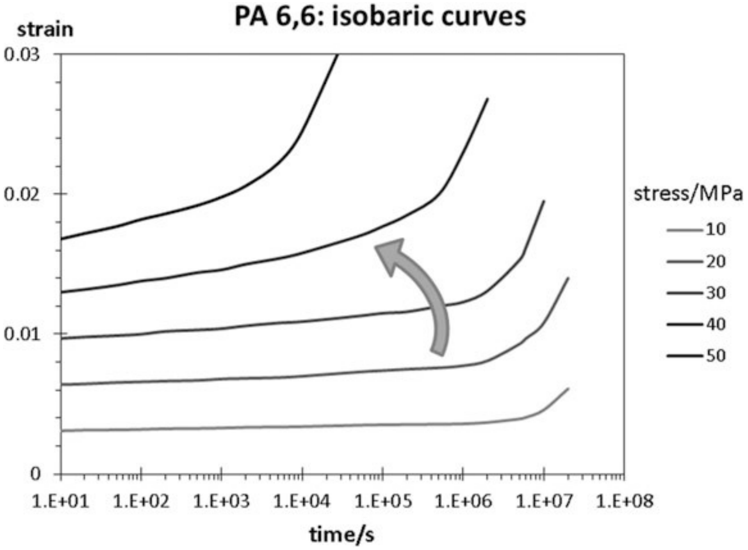


Fig. 10.13 Creep test on polyamide 6,6. *Isobaric curves* represent strain *versus* time at constant stress. The *arrow* points out to the direction of increasing stress

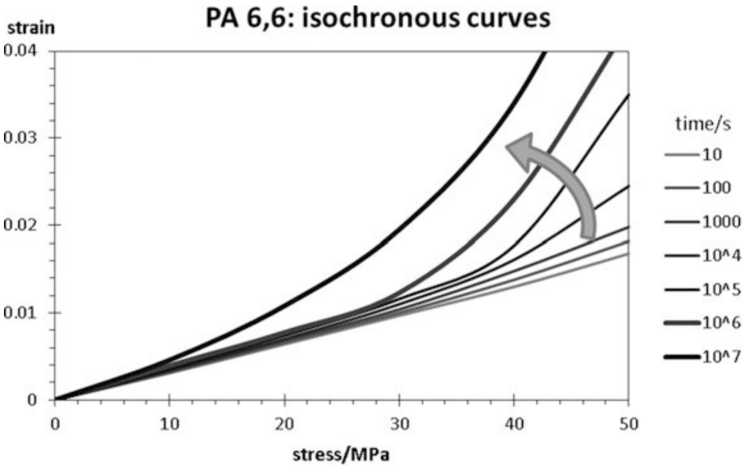


Fig. 10.14 Creep test on polyamide 6,6. *Isochronous curves* represent strain *versus* stress at constant time. The *arrow* points out to the direction of increasing time

2. *Isochronous curves* (at constant time) in which strain, or the creep compliance, are plotted versus stress at constant time. By changing the values of the stress, different isobaric curves are produced. In Fig. 10.14, the same creep data of PA66 is shown as isochronous plots.
3. *Isometric curves* (at constant strain) in which stress is plotted versus time, at constant strain. In Fig. 10.15 an isometric plot is displayed for the same PA66 data.

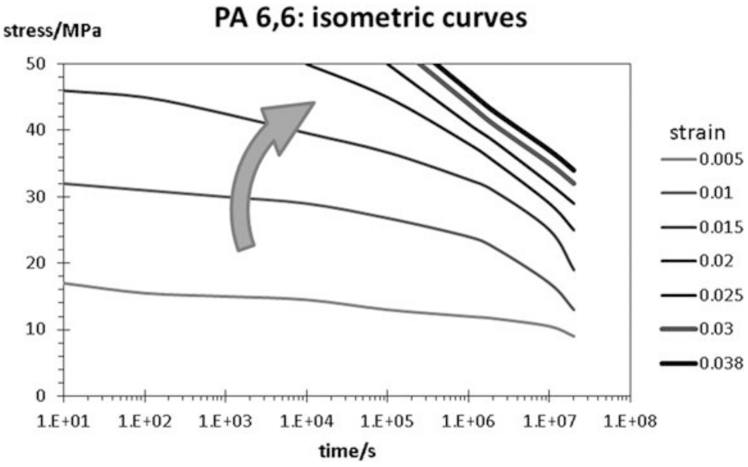


Fig. 10.15 Creep test on polyamide 6,6. *Isometric curves* represent stress *versus* time at constant strain. The *arrow* points out to the direction of increasing strain

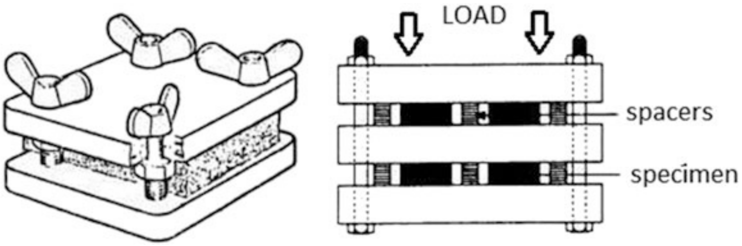


Fig. 10.16 Permanent deformation test for flexible foams

Permanent Deformation

Creep in elastomers and foams can be evaluated using tests that measure permanent deformation under compression or under tension (tensile test).

Permanent deformation under compression—This test makes it possible to test the residual deformation of flexible foams and elastomers previously subjected to a constant load for a given period of time. The test (ISO 1856) consists of compressing a foam specimen with standard dimensions up to 50, 75 and 90 % of its original size or 22 h at a temperature of 70 °C. Afterwards, the load is removed and the specimen is allowed to rest for a certain amount of time at 23 °C and its thickness is measured again. Permanent deformation is expressed by the percentage of thickness lost compared with the original amount. The compression device consists of two rigid, flat metal plates and a set of spacers that make it possible to keep the plates parallel at previously established distances (Fig. 10.16).

In elastomers, permanent deformation (ASTM D395-B) is measured by the decrease in thickness of a standard sample subjected to a given strain for a certain time; permanent deformation is measured 30 min after the stress is removed.

Permanent deformation under tension—To determine the permanent deformation rate under tension, a given strain is produced in a specimen with standard dimensions for 24 h at a well defined temperature. At the end of the test, the specimen is unloaded and allowed to rest for 30 min, and the residual deformation is measured.

Fatigue Resistance

Fatigue resistance in dynamic compression is normally expressed by the number of cycles that a specimen can withstand until rupture and by the amplitude of the cyclic load applied.

Flexible foams—The dynamic fatigue test (ISO 3385) for seatings is designed to evaluate the durability of foams and successfully reproduces seating's behaviour during use (Fig. 10.17 (a)). In this test, a standard sample measuring 380 × 380 × 50 mm is repeatedly compressed by a 750 N force at a frequency of 70 cycles per minute for 80,000 cycles. The thickness and hardness are measured before and after the test, and the percentage of loss is used to evaluate fatigue

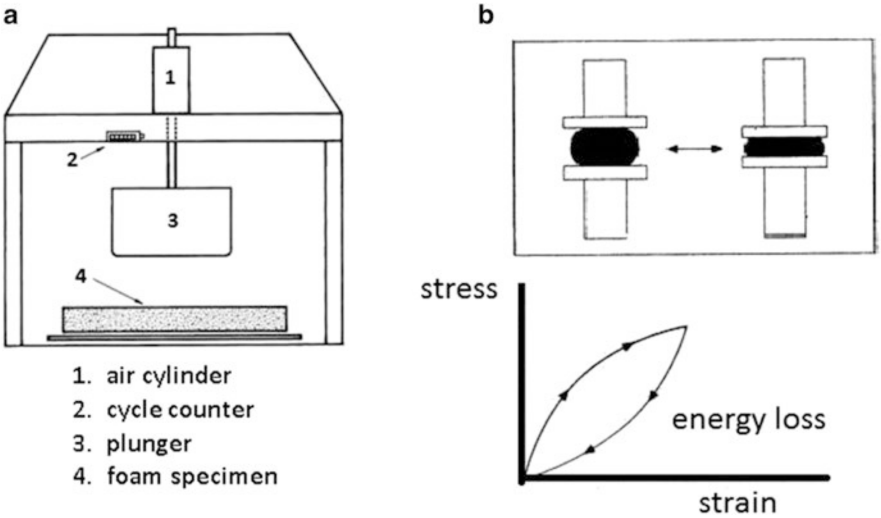


Fig. 10.17 (**a**) Fatigue test of foams in compression. (**b**) Compression test of elastomers and hysteresis cycle

resistance. Depending on the results obtained, foams are selected for different types of applications.

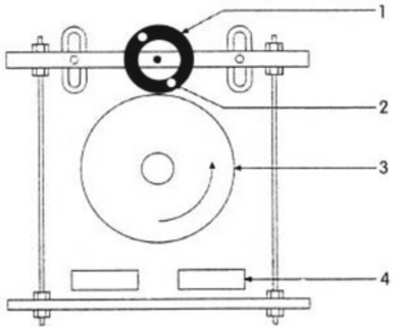
Elastomers—A specimen (Fig. 10.17 (b)) is compressed cyclically between two plates at a given frequency. The energy dissipated in the hysteresis cycle is measured throughout the test, and it is equal to the area between the load and release curves. The internal temperature of the specimen is monitored using a thermocouple inserted into the elastomer. Determining elastomers' resistance to dynamic fatigue through flexure and semi-rigid foams with full skin is described in standard ISO 132.

Abrasion Resistance

Abrasion resistance measures the material's ability to resist wear produced by friction, normally determined by the loss of weight, volume or thickness of a specimen that suffered friction against a certain abrasive material, under a specific load (ASTM D1242). Polyurethanes normally have high results for abrasion resistance.

Heating by Hysteresis

Heating by hysteresis is evaluated by the increase in temperature of a specimen subjected to a series of deformation and recovery cycles (ASTM D623). Since no elastomer is perfectly elastic, repeated deformation cycles generate heat, such as cyclical compression and relaxation cycles in a rotating tyre. The energy dissipated per unit of time depends on the frequency and load, the temperature and the dissipative part of mechanical susceptibility. Figure 10.18 shows dynamic testing



1- PU specimen attached to one rotating steel axis

2- thermocouple

3- rotating steel cylinder

4- static load applied to the contact between specimen and steel cylinder

Fig. 10.18 Equipment for dynamic testing of elastomers; specimens may be wheels or tyres

apparatus for wheels, which is used to evaluate PU elastomers. In this test, the tyre is attached to a steel central axis and rotates at a constant speed under a growing load until the temperature increases enough to cause the polymer to decompose.

10.6.1.4 Properties of Cellular Materials

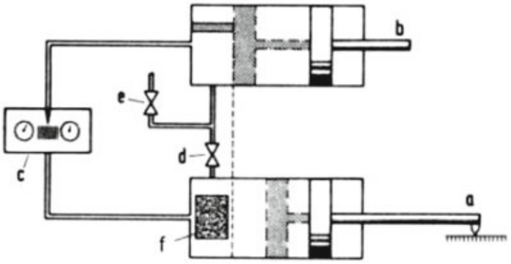
The cellular structure and the formation of transversal cells, the size and distribution of sizes of the cells all significantly influence the properties of PU foams. An estimate of the number of cells by unit length can be made using a microscope (optical or electronic). For evaluation of the anisotropy of foam, the number of cells per unit length must be measured in two perpendicular directions. A better view of the interior of the cellular structure can be obtained by using scanning electron microscopy, which shows the three-dimensional relationships between transversal cells and cellular membranes. Some authors have studied the correlations between mechanical properties, with the help of models based on the parameters of the cellular structure, and the experimental results often agree with the amounts deduced. The methods for determining some properties of cellular materials, such as apparent density, the fraction of open and closed cells and cellular structure, will now be described.

Apparent Density

PU cellular materials are characterised by their apparent density and their properties. Apparent density expression is used for cellular materials due to the fact that their density is calculated with the volume of the expanded material and not just the volume of the solid polymer (ASTM D792).

Determining Open and Closed Cells Content

In rigid foams, the proportion of closed cells affects several important physical properties, such a thermal conductivity, water vapour permeability and water absorption. The proportion of closed cells is determined by the volume of air displaced by a foam specimen with known dimensions. The foam is placed in a closed chamber and the chamber's volume is then increased by a known amount.



a) test chamber

b) comparison chamber

c) differential air pressure measurer

d) adjustment valve

e) release valve

f) specimen

Fig. 10.19 Determination of the open/closed cells content

The decrease in the test chamber pressure is measured and compared to the one for gas expansion in an empty chamber (Fig. 10.19). The closed cell content is proportional to the air displacement contained in the test sample and is calculated by applying the Boyle-Mariotte law. The open and closed cells content can also be measured by using a gas pycnometer.

10.6.1.5 Thermal Properties

The ability to transfer heat, that is, conduct heat, is measured by thermal conductivity. Changes in size, due to temperature changes, are estimated through thermal expansion and thermal dimensional stability. On the other hand, it is important to know the crystalline melting temperature (T_m) and glass transition temperature (T_g).

Thermal Expansion

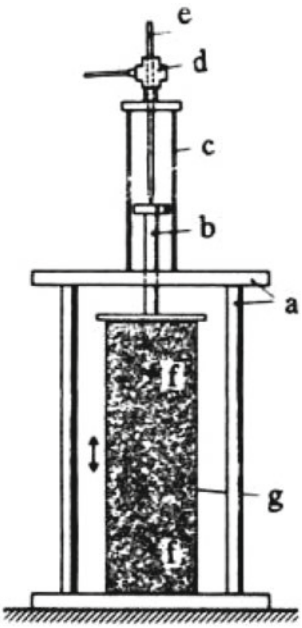
In buildings that use rigid foams for thermal insulation, knowing its thermal expansion (variations in volume with temperature) between –40 and 100 °C is extremely important. The equipment described in Fig. 10.20 makes it possible to continually check the thermal expansion coefficient in the –40 to 80 °C range in specimens with dimensions 200 × 50 × 50 mm. In this test, a compressive stress of about 300 Pa is applied. The average determination error is ±3 %.

Thermal Conductivity

The low thermal conductivity of rigid foams is probably their most important physical property. In the ISO 2582 method, two foam samples are placed in contact with opposite surfaces of an electrical heating plate (Fig. 10.21). The current through the heating plate is adjusted until stationary state conditions are achieved. In this state, the power dissipated is the same as the heat flow through the samples. The thermal conductivity is then calculated from the temperature gradient, sample dimensions and the power dissipated.

Thermal Dimensional Stability

PU rigid foams contain a gaseous mixture of expansion agents in their closed cells. As temperature changes, the closed cells are compressed by air pressure at low



a) quartz structure

b) quartz piston

c) quartz tube

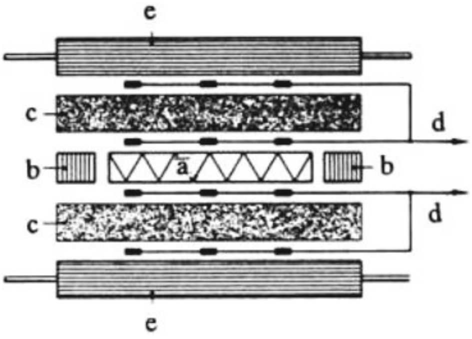
d) induction recorder

e) immersed reinforcement

f) thermal element

g) specimen

Fig. 10.20 Determination of the thermal expansion coefficient



a) heating plate

b) heating ring

c) test sample

d) thermocouple

e) cooling plates

Fig. 10.21 Method of measurement of thermal conductivity (ISO 2582)

temperatures or expanded by internal gas pressure at high temperatures. To determine thermal dimensional stability (ISO 2796), the variations in linear dimensions of the foam are determined after being stored for a certain period of time under specific environmental conditions (preferably dry air and temperatures of –55, –25, –10, +100 or +125 °C).

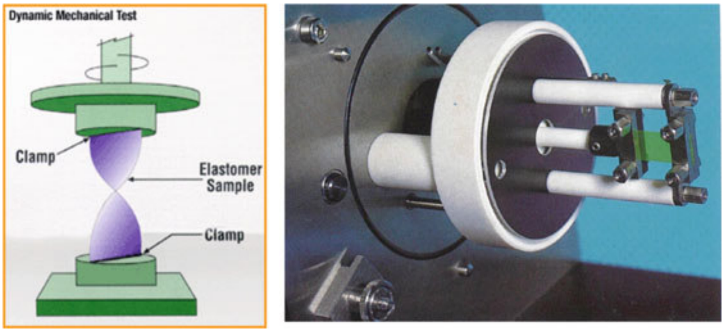


Fig. 10.22 Dynamic mechanical tests in torsion mode (*left*) and in tension mode (*right*)

Dynamic Mechanical Thermal Analysis

Dynamic mechanical analysis (DMA) measures the mechanical response of a material subjected to a harmonic stimulus (stress or strain) under accommodation conditions: the response depends on the frequency and size of the stimulus (see Fig. 10.22). If the stimulus is stress, the response is strain (stress-controlled experiment); if the stimulus is strain, the response is stress (strain-controlled experiment).

For a perfectly elastic material, stress and strain are in phases. For a viscous material, stress and strain are out of step by 90 °. For a viscoelastic material, the phase lag between stress and strain is found between these two limits (see Fig. 10.23).

Dynamic mechanical thermal analysis (DMTA) measures the mechanical response of a material subjected to a harmonic stimulus (in accommodation), within a certain temperature range. Normally, the specimen is cooled to a sufficiently low temperature, which can reach -150 °C. The specimen is then heated at a controlled heating rate: around 1–5 °C per minute. The test is carried out normally during heating.

The quotient between stress and strain is a complex quantity, the *complex modulus* $G(\omega) = G'(\omega) + i \times \mathrm{G}''(\omega)$. The real part, $G'(\omega)$, called “elastic modulus”, is proportional to the maximum amount of elastic energy absorbed during a cycle; the imaginary part, G'' (ω), named “dissipative modulus”, is proportional to the dissipative energy during a cycle. The complex modulus is strongly dependent on temperature and frequency; using that dependency the different relaxation processes associated to viscoelastic behaviour can be measured quantitatively (Figs. 10.24, 10.25, 10.26).

The phase lag angle δ between stress and strain, is frequency dependent; its value is given by

$$\tan \delta(\omega) = \frac{G''(\omega)}{G'(\omega)}$$

Plots representing the temperature dependence of tan δ are often used to identify the characteristic temperature of glass transition, T_g.

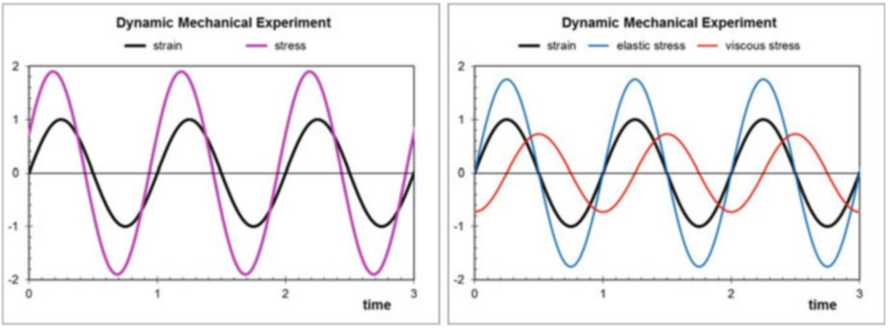


Fig. 10.23 Time dependence of strain and stress in a dynamic mechanical test (*left*). Time dependence of strain, elastic stress (in phase with strain) and dissipative viscous stress (in phase with rate of strain) in a dynamic mechanical test (*right*)

The DMTA test makes it possible to obtain a substantial amount of information on structure, morphology, phase transitions and relaxations and a material's dynamic behaviour. A list of the properties and quantities that can be obtained by DMTA analysis is provided as follows:

Semicrystalline Polymers

- Temperature and intensity (relaxation strength) of glass relaxation or glass transition and secondary sub-glass relaxations
- Temperature and intensity of secondary transitions related to melting

Fig. 10.24 DMA/DMTA equipment at the Rheology Laboratory of IST-UL

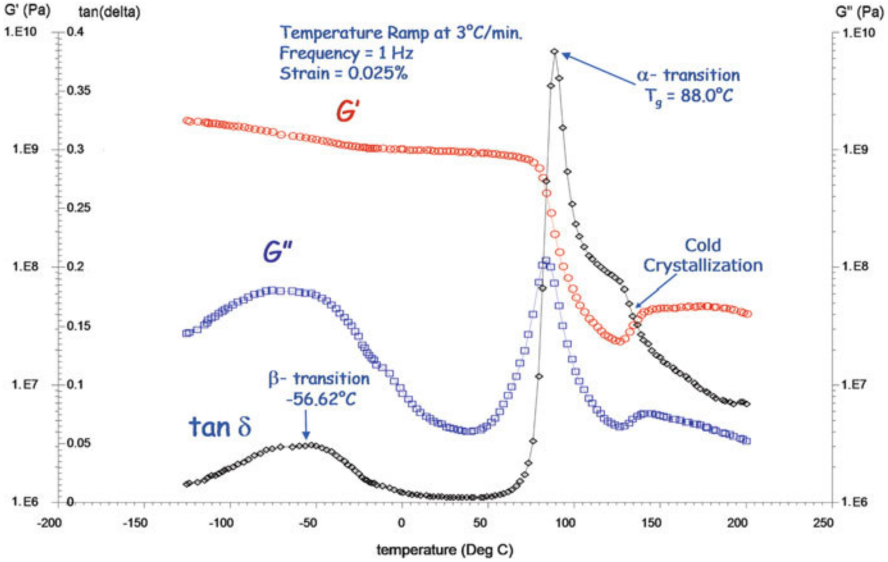


Fig. 10.25 Dynamic mechanical analysis of a polyester (PET). The temperature range varies between −150 and 250 °C

- Effect of the type and concentration of plasticisers on temperature and intensity of glass and subglass transitions
- Melting point (crystalline) and distortion/softening temperature; crystallisation kinetics (isothermal and non-isothermal); estimation of the degree of crystallinity from the jump in modulus at the glass relaxation T_g

Elastomers

- Morphological information on the crystalline phase, anisotropy and degree of molecular orientation
- Degree of crosslinking: based on the representation of tan δ, in the case of weak crosslinking, from $G'(\omega)$, in the case of tight crosslinking; heterogeneity of cross-linking points and presence of a microgel phase in highly crosslinked polymers
- Elastomer plateau modulus
- Gel point
- Effect of addition of fillers; characterising the degree of adhesion and friction between particles in elastomers with (active or inert) fillers

Thermosetting Polymers

- Kinetics of crosslinking, follow-up of crosslinking the cross-linking process, gel point and post-cure kinetics
- Matrix-fibre adhesion in thermosetting matrix composites
- Copolymers: Polymer mixtures

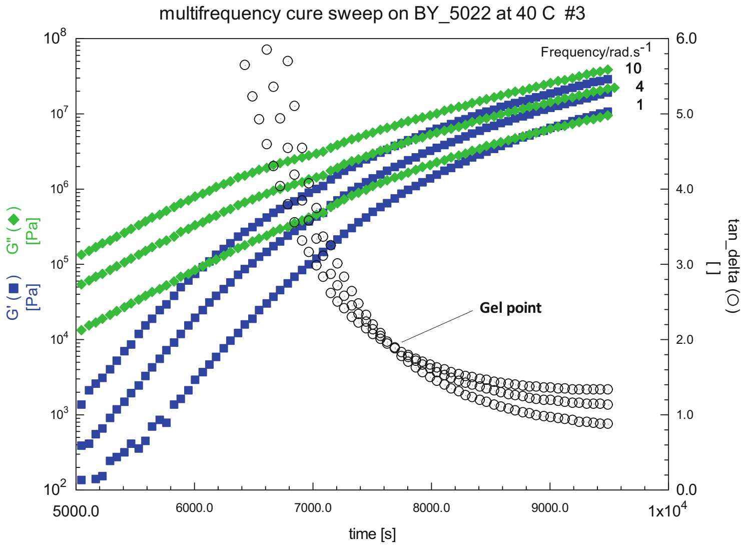


Fig. 10.26 Follow-up of the cure of an epoxy resin by dynamic mechanical analysis. At the gel point tan δ is independent of frequency; the gel point occurs 7,686 s after start-up of the cure

- Temperature and intensity (relaxation strength) of glass transition and secondary subglass transitions of different components
- Heterogeneity of the copolymer composition based on the width of tan *δ* in glass transition; compatibility of the blocks
- Morphology of the phases in block copolymers; inversion of phases in block copolymers; characterisation of copolymers: statistical, block, etc.
- Morphology, composition and concentration of components in polymer blends

General Properties

- Estimate of mechanical properties: impact resistance, toughness, creep behaviour and stress relaxation
- Damping factor for mechanical and acoustic vibrations; prediction of coefficient of friction in bearings
- Stress-strain behaviour temperature dependance
- Predicting rheograms in melted materials
- Evaluating and monitoring physical, chemical and thermo-oxidative degradation in polymer materials and polymer matrix composites

10.7 Chemical and Physical–Chemical Tests

This section describes how to establish some chemical and physical–chemical properties, such as accelerated ageing, water vapour permeability and the stability of gases, liquids and solids.

10.7.1 Accelerated Ageing Tests

All irreversible alterations to physical and chemical properties that take place in the life time of a part or a specimen are ageing processes. Thermodynamically unstable states evolve into more stable ones. The increase of crystallinity due to secondary crystallisation, the ordering of rigid polyurethane segments, phase segregation in multiphase systems and the relaxation of internal stresses produced during processing, are examples of internal ageing processes. The influence of the environment conditions can lead to the formation of fatigue cracks, changes in dimensions due to swelling, thermo-oxidative, photo-oxidative or hydrolytic degradation. There are multiple standard testing procedures for accelerated ageing (heat, moisture, visible and ultraviolet irradiation) currently used in quality control.

10.7.2 Stability under Gases and Liquids

The action of chemical products may cause degradation of the material. Degradation mechanisms include chemical reactions (e.g. hydrolysis), swelling due to solvents, stress corrosion, cracking, etc. Assessment of the stability under water and water vapour at high temperatures is very important for polyesters, polyurethanes and polyamides, for example. Ageing is normally carried out in duly conditioned chambers or in autoclaves. As an example, ageing due to water vapour is produced in an autoclave (ISO 2440); specimens are kept in air saturated with water vapour for 20 hours at 85°C, for 3 hours at 105°C or for 5 hours at 125°C. Quantification of ageing is done by comparison of the values of a chosen material function or material constant (e.g. the Young modulus) before and after ageing.

Appendix: The Three-Litre House

The three-litre house is a house measuring 100 m^2 area and was designed and produced by BASF. It consumes the equivalent of 300 L of fuel per year, or 3 L/m^2 per year.The comparison between the cost of running the 3-L house and a traditional house with the same area gives the following results:

- Reduction in energy consumption: 2,000 L to 300 L of fuel
- Reduction in carbon dioxide emissions (CO_2): 6 tonnes to 1 tonne
- Heating costs: €1,000 to €150 (Fig. 10.27)

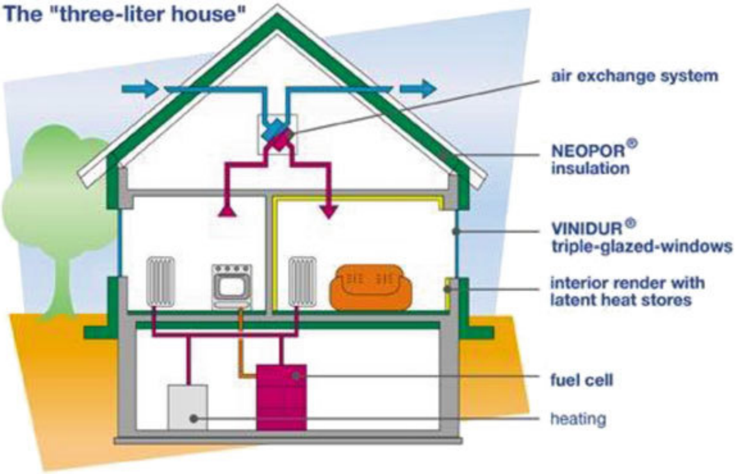


Fig. 10.27 Diagram of the "three-litre house"

The reduction in costs is achieved by:

- Thermal insulation in the walls and ceilings using high-performance polystyrene foam ($K<0.17$ W m^{-2} K^{-1})
- Heat storage system using the latent heat in polymeric waxes
- Thermal windows: PVC frames with triple windows
- Passive use of solar energy
- Generation of energy using fuel cells
- Ventilation system

One of the characteristics of the three-litre house is the abundant use of polymeric materials:

- *Polystyrene*: in high-performance thermal insulation foams
- *Polypropylene*: ventilation systems, energy control system, thermal insulation foam, solar panels
- *Polyurethane*: in the form of foams
- *Polyvinyl chloride*: ventilation system, energy control system, window frames, solar panels
- *Polyethylene*: ventilation system, floor heating
- *Polybutylene*: floor heating
- *Engineering thermoplastics*: ventilation system, fuel cells, energy control system, solar panels

Bibiliography

A: General

Argon AS (2013) The physics of deformation and fracture of polymers. Cambridge University Press, New York

APME Association of Plastics Manufacturers in Europe. Plastics a material of choice in building and construction (report) www.plasticseurope.org.

Azapagic A, Emsley A, Hamerton I (2003) Polymers, the environment and sustainable development. Wiley, Chichester

Boyd RH, Smith GD (2007) Polymer dynamics and relaxation. Cambridge University Press, Cambridge

Brockmann W, Geiß PL, Klingen J, Schröder B (2009) Adhesive bonding. Wiley-VCH, Weinheim

Brown R (ed) (1999) Handbook of polymer testing. Marcel Dekker, New York

Brown R (2006) Physical testing of rubber, 4th edn. Springer, New York

Driscoll SB (2004) The basics of testing plastics. ASTM, West Conshohocken

Elias HG (1997) An introduction to polymer science. Weinheim, VCH

Gupta N, Pinisetty D, Shunmugasamy VC (2013) Reinforced polymer matrix syntactic foams. Springer, New York

Hellerich W, Harsch G, Haenle S (1989) Guia de Materiales Plásticos. Hanser, Barcelona

Kaplan WA (ed) (1999) Modern plastics world encyclopedia 2000. McGraw-Hill, New York

Lampman S (ed) (2003) Characterization and failure analysis of plastics. ASM International, Materials Park

Menard KP (2008) Dynamic mechanical analysis, 2nd edn. CRC Press, New York

Mills NJ (2007) Polymer foams handbook. Butterworth-Heinemann, Oxford

Riande E, Diaz-Calleja R, Prolongo MG, Masegosa RM, Salom C (2000) Polymer viscoelasticity. Marcel Dekker, New York

Saldivar-Guerra E, Vivaldo-Lima E (2013) Handbook of polymer synthesis, characterization, and processing. Wiley, Hoboken

Shah V (2007) Handbook of plastics testing and failure analysis. Wiley, Hoboken

Swallowe GM (1999) Mechanical properties and testing of polymers. Springer Science, Dordrecht

Woods G (1987) The ICI polyurethanes book. Wiley, New York

Zeng H (ed) (2013) Polymer adhesion, friction, and lubrication. Wiley, Hoboken

B: Specialised

BASF—The 3-liter-house www.3lh.de.

Baskaran A, Chen Y, Vilaipornsawai U (1999) New dynamic wind load cycle to evaluate mechanically attached flexible membrane roofs. J Test Eval 27:249–65

Booth RJ, de Rushie C, Liu K (2002) Protection of foam plastic thermal insulation in low sloped roofing systems. J Thermal Envelope Build Sci 25:255–74

Diogo AC (2001) Reologia dos Elastómeros. In: Covas JA, Diogo AC, Gomes de Castro A (eds). Reologia e suas Aplicações Industriais. Lisbon, Instituto Piaget, pp 273–309

Diogo T, Barbosa T, Bordado J (2002) Rheological behaviour of bitumens modified with reactive polyurethanes. In: Correia AG, Branco F (eds) Proceedings 6th International conference on the bearing capacity of roads, railways and airfields, vol 2. Lisse, A.A. Balkema, pp 831–838

Girois S, Schipper PS (2001) Enhanced weatherability of exterior PVC building products. J Vinyl Addit Technol 7:61–6

Lau KT, Zhou LM, Tse PC, Yuan LB (2002) Applications of composites, optical fibre sensors and smart composites for concrete rehabilitation: an overview. Applied Composite Materials 9:221–47

Lohman RJ (2002) Construction adhesives: what the future holds. Adhesives Age 45:46

Nordin H (2003) Fibre reinforced polymers in civil engineering, Thesis, Lulea University of Technology, Sweden

Reis JML, Ferreira AJM (2003) Fracture behaviour of glass fiber reinforced polymer concrete". Polymer Testing 22:149–153

Srivastava A, Agarwal RK, Singh P (2001) Sustainable development of plastics as construction materials. Pop Plast Packag 46:71–4

Fibre-Reinforced Polymer (FRP) Composites

11

João Ramôa Correia

Abstract

The first part of this chapter focuses on the constituent materials (fibres and polymeric matrices), manufacturing processes, general properties and field of application of fibre reinforced polymer (FRP) composites used in civil engineering applications. Subsequently, detailed information is provided about the following three main types of FRP shapes used in structural applications: (1) glass fibre-reinforced polymer (GFRP) pultruded profiles; (2) FRP rebars and (3) FRP strengthening systems. For each of these three main FRP typologies, the following aspects are discussed: geometries, typical physical and mechanical properties, advantages and difficulties compared to more traditional construction materials, field of application, application process and connection technology, and regulation.

Keywords

Fibre reinforced polymer • Composites • Fibres • Polymeric matrices • Pultrusion • Hand layup • GFRP pultruded profiles • FRP rebars • FRP strengthening systems • Geometries • Typical properties • Field of application • Application process • Regulation

11.1 Introduction

Throughout history, the major breakthroughs in civil engineering have usually stemmed from the use of new materials. The application of cast and wrought iron in the eighteenth and nineteenth centuries was a decisive factor for the industrial

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M.C. Gonçalves, F. Margarido (eds.), *Materials for Construction and Civil Engineering*, DOI 10.1007/978-3-319-08236-3_11

revolution. Later, in the second half of the twentieth century, the application of concrete also contributed decisively for the rapid reconstruction which took place after the Second World War [43].

Presently, some of the most important challenges that civil engineering is facing are associated with the maintenance and reparation costs of structures built with traditional materials, most often steel, reinforced concrete and timber, which have dramatically increased in the last few years. As an example, in the United States of America (USA), according to the 2013 American Society of Civil Engineers (ASCE) report for America's infrastructure, almost 25 % of the 600,000 bridges are either structurally deficient (in most cases due to corrosion-related anomalies) or functionally obsolete [5]. It has also been estimated that 40 % of the bridges built in the USA after 1945 need to be replaced until the end of this decade [37].

The durability problems associated with traditional materials have led to changes not only in the design practice but also in the codes and standards, which, in general, presently already take into account such problem. Together with the needs of higher speeds of construction and increasing functionality demands, those durability concerns have also had a stimulating effect in the development of innovative structural solutions, comprising new materials with high mechanical performance but at the same time lighter, less prone to the degradation caused by aggressive environmental agents and requiring less maintenance during their service life.

Within these new materials, fibre-reinforced polymers (FRP) are presently assuming a particular relevance. These composite materials are basically constituted by a fibrous reinforcement (generally glass, carbon or aramid) embedded in a polymeric matrix (most often made of polyester, vinylester or epoxy). Initially developed by the naval and aerospace industries in the decade of 1940, FRP materials then expanded to several other industries, among which the petrochemical and automotive industries. In those fields of application, FRP materials proved to combine very good mechanical performance, lightness and improved durability, even when submitted to relatively aggressive environments. Such advantageous characteristics enabled a growing interest by the construction industry, where FRP materials have been finding increasing applications since the decade of 1980 [6].

Section 11.2 of this chapter presents a brief historical overview concerning the development of FRP materials. Section 11.3 presents the general characteristics of FRP materials, their constituent materials, the philosophy associated with their development and their main field of application in civil engineering. This section discusses also some critical issues related with FRP materials, namely their durability, sustainability and fire behaviour. The following sections address specific aspects concerning the three typologies of FRP materials more frequently used in civil engineering applications, glass fibre-reinforced polymer (GFRP) pultruded profiles (Sect. 11.4), FRP rebars (Sect. 11.5) and FRP strengthening systems (Sect. 11.6). For each typology, the following aspects are presented and discussed: structural shapes and geometries, typical physical and mechanical properties, advantages and difficulties in their use, preferential field of application, connection technology (whenever applicable), application process and regulation.

11.2 The Use of FRP Materials Throughout History

Since the antiquity, man attempted to combine different materials in his constructions, trying to make use of the best properties and advantages of each material. As an example, in Mesopotamia, there are records from 5000 B.C. of the use of mud reinforced with straw, in order to reduce the cracking during the drying process of the bricks [53]. This ancient composite system has obvious similarities with modern fibre reinforcement polymer (FRP) materials, with the mud performing as the polymeric resin and the straw behaving as the fibre reinforcement. While the concept of composite materials is known for several centuries, the incorporation of fibre reinforcements in a polymeric matrix is a relatively recent technology, which was only enabled with the development of the plastic industry, after the beginning of the twentieth century.

The first-known application of FRP materials dates back to the 1930s, when these materials were used in the skull of a boat, in the scope of an experimental project [14]. The widespread use of modern composite materials in structural applications occurred only during the 1940s, when glass fibre-reinforced polyester matrices were used in boat skulls and radomes (radar cover) [60]. During this early period of development, the use of FRP materials was closely connected to the defence industries, particularly for naval and aerospace applications. These industries have always been very important in driving forward the development of composite materials.

In 1948, FRP materials were first used in the oil industry, which constitutes since then one of the main consumers of composite materials, with applications in pipework and panelling for both floors and walls of off-shore platforms. Other industries with particular requirements (namely, resistance to aggressive environments and thermal and electromagnetic insulation) have also applied FRP materials since the 1950s, such as the chemical industry, the paper industry, the water and waste treatment industries and electrical stations [14].

The first interest of the construction industry on FRP materials dates back to the 1950s and 1960s, when approximately 70 prototype houses were built. Most of these first FRP buildings were single-storey and none comprised more than two storeys[1] [62]. Architectural concepts were not at all traditional, with most of these modern buildings being modular and using form-active structures to overcome the low stiffness of the material. At this stage, FRP materials were essentially used in the façades, often integrated in a primary structure made of traditional materials [38]. Figures 11.1, 11.2, and 11.3 show three examples of these early achievements:

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[1] Tracy [62] presents an excellent overview of the historical development of FRP buildings and building systems in these early stages.

Fig. 11.1 Monsanto house of the future

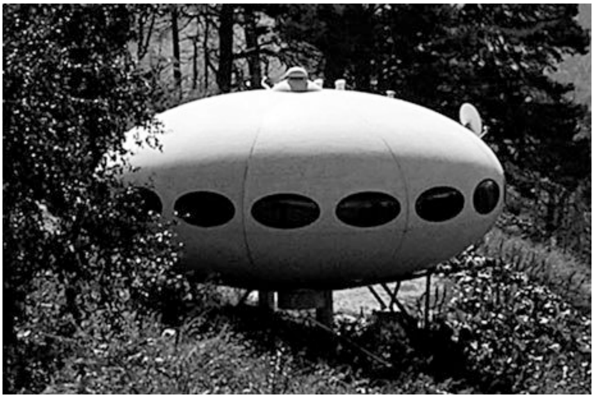

Fig. 11.2 Futuro house

the *Monsanto House of the Future*, the *Futuro House* and the *Icosahedron Classroom*. Unfortunately, these pioneering applications ended up being abandoned, not only due to financial reasons but also due to their rejection by the architectural community, for which the lack of technical information also gave an important contribute.

The automotive industry (Fig. 11.4a) introduced composite materials in its components, for the first time, in the beginning of the 1950s. In the decade of 1970, the automotive industry was already the main consumer of composite materials, surpassing the naval industry [14].

In the decade of 1960, the first advanced composite materials, made of high strength and modulus fibres (such as carbon and aramid), started to be manufactured in order to meet the higher performance challenges of space exploration and air travel. However, due to the relatively high cost of such solutions, limited application was seen outside the market niches of aerospace and defence industries.

In the decade of 1970, as a consequence of the energetic crisis, the composites manufacturing industry made an effort to reduce the production costs, which later

Fig. 11.3 Icosahedron classroom [38]

Fig. 11.4 Use of composite materials in (**a**) automotive, (**b**) aviation and (**c**) naval recreation industries [27]

enabled to broaden their field of application to other markets, such as aviation (Fig. 11.4b) and naval (Fig. 11.4c) recreation industries, and also several sporting goods, including very diverse products, such as fishing rods, tennis racquets, golf clubs and ski equipment.

In the decade of 1980, new manufacturing processes were developed, allowing to produce carbon fibres with excellent mechanical properties at very competitive costs. At this stage, it was thought that the carbon fibres production would surpass that of glass fibres. However, presently, glass fibres are still used in the vast majority of composite materials for structural applications.

During the late 1980s and the early 1990s, the cost reduction of FRP materials (associated with the technological evolution of manufacturing processes, such as pultrusion) occurred together with the renovation needs of a growing number of structures, especially those located in highways, with either durability-related problems or increasing functionality demands. The development of pilot projects, supported by both industry and governmental agencies, in parallel with the growing interest of research laboratories, contributed to an increasing and renewed acceptance of such solutions in the construction industry. Since then, a wide range of products has been developed: bars and prestress cables for internal concrete reinforcement; strips, laminates and wraps for external reinforcement of concrete structural elements; prestress cables for suspended bridges; structural profiles and cellular panels. All these solutions have had an increasing number of applications, either in the rehabilitation of existing constructions or in new construction.

11.3 General Properties of FRP Materials

Composite materials result from the combination of two or more materials which, when used separately, may not present adequate properties to be used as construction materials but, when combined and maintaining an identifiable interface surface, may constitute a new material that symbiotically merges the best properties of the original materials.

FRP materials are constituted by two phases: (1) the fibre reinforcement, which is responsible for the mechanical performance of the material, providing most of its strength and stiffness and (2) the polymeric matrix, which acts as the *glue* of the composite material, guaranteeing the load transfer between the fibres and also between the applied loads and the composite itself. In addition to the resin, the polymeric matrix of FRP materials often incorporates fillers and additives that may reduce production costs, improve the manufacturing process itself and improve specific properties of the final product.

Section 11.3.1 presents the characteristics of the constituent materials of FRP composites. The judicious combination of the constituent materials has enabled the development of a wide range of products that have been used in very different structural applications, featuring several advantages when compared to traditional materials. In Sect. 11.3.2 the philosophy subjacent to the development of FRP materials is briefly discussed. Section 11.3.3 describes the manufacturing processes used to produce FRP composites. Finally, Sect. 11.3.4 presents examples of developed products and their field of application.

11.3.1 Constituent Materials

11.3.1.1 Fibres

The main role of the fibre reinforcements is to support the mechanical solicitations of the structural elements, providing enough strength and stiffness along the direction in which they develop. The most commonly used types of fibres in commercial applications include glass, carbon and aramid.[2] The physical, mechanical and thermal properties of these fibres are presented in Table 11.1.

Glass fibres are the type of fibre reinforcement most frequently used in the construction industry, namely in GFRP pultruded profiles, bars and skins of

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[2] Basalt fibres recently started to be commercially produced for FRP materials.

Table 11.1 Typical characteristics of main fibre reinforcements (adapted from [47, 7])

Property	Test standard	E-Glass	Carbon	Aramid
Tensile strength [MPa]	ISO 5079, ISO 11566, ASTM C 1557, ASTM D 2343, ASTM D 3379	2,350–4,600	2,600–3,600	2,800–4,100
Elasticity modulus in tension [GPa]		73–88	200–400	70–190
Maximum strain in tension [%]		2.5–4.5	0.6–1.5	2.0–4.0
Density [g/cm^3]	ISO 1889, ISO 10119, ASTM D 1577	2.6	1.7–1.9	1.4
Thermal expansion coefficient [10^{-6}/K]	ISO 7991	5.0–6.0	Axial: -1.3 to -0.1	-3.5
			Radial: 18.0	
Fibres diameter [μm]	ISO 1888, ISO 11567	3–13	6–7	12
Fibres structure	–	Isotropic	Anisotropic	Anisotropic

sandwich panels. Their main advantage stems from the combination of high strength and relatively low cost. The main drawbacks of glass fibres result from their low elasticity modulus, reduced long-term strength (stress rupture) and susceptibility to moisture and alkaline environments [47]. Among the different types of glass fibres (with the designations E, S, AR, C), they all present the same elasticity modulus but have different mechanical strength and durability performance. The conventional E-glass fibres, with good electrical insulation properties, are by far the most used corresponding to about 80–90 % of the commercialized products [1]. Type S fibres have improved mechanical resistance but are far more expensive (3–4 times) than E-glass fibres and are essentially used in the aerospace industry. Type AR fibres, with increased zirconia content, offer improved performance in alkaline environments and therefore can be used in cementitious composites, such as GRC (glass fibre reinforced concrete); and C-glass fibres present an improved corrosion resistance [8], but are rarely used in civil engineering applications.

Carbon fibres are generally used in strengthening applications in the form of CFRP strips, sheets, bars and prestress tendons. They present high tensile strength and elasticity modulus, low self-weight, high fatigue and creep resistance and excellent chemical resistance [14, 60]. Their main drawbacks stem from the high costs of production, which usually involves large amounts of energy [47]. Carbon fibres are available in several grades, including standard modulus (the conventional grade, listed in Table 11.1), and several improved grades that include intermediate modulus, high modulus and ultra-high modulus [7].

Aramid fibres are stronger than glass fibres and present an elasticity modulus that is 50 % higher [14]. In addition, these fibres have great potential for industrial applications requiring high energy absorption (such as automotive crash attenuators,

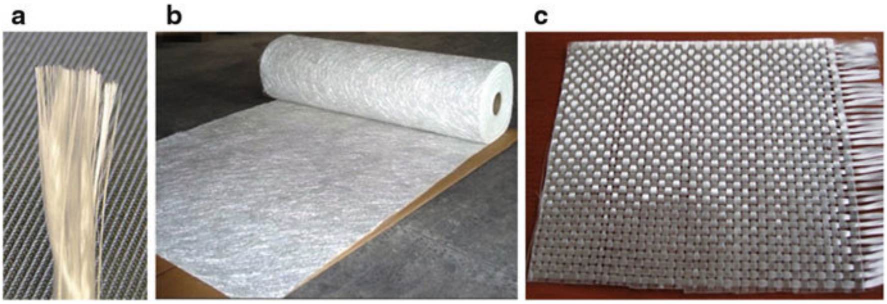

Fig. 11.5 Examples of available forms of fibre reinforcements: (**a**) rovings, (**b**) chopped strand mat, (**c**) biaxial woven fabric

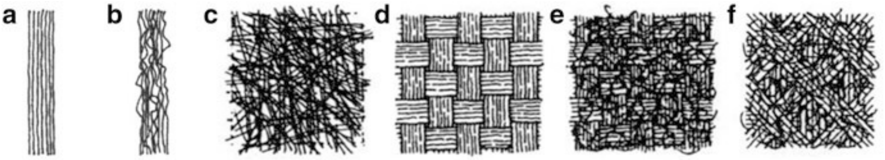

Fig. 11.6 Different types of mats: (**a**) rovings, (**b**) yarns, (**c**) continuous strand mat (random fibre orientation), (**d**) biaxial woven fabric (0°/90°), (**e**) complex mat (0°/90° weave + random fibre orientation), (**f**) bidirectional complex mat (0°/45°/90° weave + random fibre orientation) (adapted from [31])

bulletproof vests and helmets) due to their good tenacity and toughness properties [7]. The main disadvantages of aramid fibres are the relatively low compressive strength (500–1,000 MPa), the susceptibility to stress rupture (reduced long-term strength) and the high sensitivity to UV radiation [47]. The potential interest for civil engineering applications is detracted from the above disadvantages.

The different types of fibres mentioned above can be used to reinforce FRP materials in various forms, namely short fibres (chopped), typically with lengths ranging from 3 to 50 mm, and almost parallel bundles of continuous filaments, untwisted (rovings) or twisted (yarns) [47]. These fibre reinforcement forms can be further worked to produce textile products with various reinforcing directions. Several products can be developed, either with randomly oriented fibres, which can be short (chopped strand mat) or continuous (continuous strand mat), or with oriented reinforcement (e.g. woven and non-woven fabrics, stitched fabrics, grids and meshes), which can be biaxial (0°/90° or +45°/−45°) or triaxial (0°/+45°/−45°). Finally, all these forms can be further combined to constitute textile products with continuous oriented fibres, together with continuous or randomly oriented short fibres. Figures 11.5 and 11.6 show examples of available forms of fibre reinforcement.

In order to prevent the reinforcement from being damaged during processing and to help fibres sticking together, they generally receive a chemical superficial treatment with a constituent named sizing (typically made of starch, oil or wax). Sizings provide lubricant and antistatic properties and promote the fibre–matrix debonding since they incorporate a coupling agent. For some types of fibres (e.g. glass), sizings also improve the durability during service life, by providing protection against moisture degradation [8].

11.3.1.2 Polymeric Matrices

The mechanical performance of FRP composites relies mostly on the fibre reinforcement. However, for some types of loading, the polymeric matrixes are also responsible for carrying part of the loads, particularly those associated with transverse stresses and interlaminar shear stresses [8]. In addition, the polymeric matrix is expected to fulfil the following requirements [47]: (1) keeping the fibres in the intended position, (2) guaranteeing the load transfer/distribution between the fibres, (3) preventing the fibres from buckling when subjected to compression stresses and (4) protecting the fibres against the environmental degradation agents, such as moisture (similarly to the steel reinforcement protection provided by the concrete cover, in reinforced concrete structures).

The polymeric matrices of FRP materials are constituted by a base resin and generally comprise supplementary constituents, used to induce the polymerization reaction, to improve the material processing, to reduce the material cost and to tailor the properties of the final FRP product. These additional constituents can be divided in three groups: (1) polymerization agents, (2) fillers and (3) additives.

Resins

There are two main groups of polymeric resins: thermosetting resins and thermoplastic resins. These resins can be distinguished from one another by the way the polymer chains are connected when the polymer is in its solid form.

Thermosetting resins (that include polyester, vinylester, epoxy and phenolic) result from a polymerization chemical reaction. This reaction takes place in the presence of heat and leads to the formation of an amorphous three-dimensional cross-linked molecular structure. Due to its own irreversible nature, thermosetting resins become infusible after curing and therefore they are no longer reprocessable nor can be welded. Thermosetting resins have good fibre impregnation capacity and very good adhesive properties. In addition, they exhibit low viscosity, allowing for high processing speeds.

Thermoplastic resins (that include polypropylene, polyamide, polyethylene and polybutylene) are not cross-linked and do not suffer any chemical transformation during processing. Their molecular chains are held together by weak van der Waals forces or by hydrogen bonds. Since thermoplastic resins do not form an irreversible structure, they can be recycled and reprocessed. Compared to thermoset resins, thermoplastic resins exhibit significantly worse properties of impregnation and adhesion to the fibres and, due to their higher viscosity, are much more difficult to process, which increases the manufacturing costs.

Due to the above-mentioned features, thermosetting resins have much higher potential for civil engineering structural applications and therefore have been used in the vast majority of FRP products commercially available. Table 11.2 presents typical physical and mechanical properties of the most frequent thermosetting resins (polyester, vinylester, epoxy and phenolic). These resins are isotropic and viscoelastic materials.

Table 11.2 Physical and mechanical properties of thermoset resins (adapted from [47, 31])

Property	Test standard	Polyester	Epoxy	Vinylester	Phenolic
Tensile strength [MPa]	ISO 527, ASTM D 638	20–70	60–80	68–82	30–50
Elasticity modulus in tension [GPa]		2.0–3.0	2.0–4.0	3.5	3.6
Maximum strain in tension [%]		1.0–5.0	1.0–8.0	3.0–4.0	1.8–2.5
Density [g/cm^3]	ISO 1183, ASTM D 1505	1.20–1.30	1.20–1.30	1.12–1.16	1.00–1.25
Glass transition temperature [°C]	ISO 11357-2, ISO 11359-2, ASTM E 1356, ASTM E 1640	70–120	100–270	102–150	260

Polyester represents approximately 75 % of the resins presently used in FRP products [14]. This figure stems from the good balance between their properties (mechanical, chemical, electrical), the dimensional stability, the ease of processing (reduced viscosity, associated with a reasonable pot life, possibility of introducing changes in the matrix composition during polymerization reactions) and the relatively inexpensive price.

Epoxy resins are generally used in structural strengthening applications with particularly stringent requirements (in terms of strength, stiffness, service temperature and durability) either combined with carbon fibres (strips, sheets, etc.) or applied separately as structural adhesives. Compared to polyester, although epoxy resins are more difficult to process due to their higher viscosity and require a longer cure, they present considerably lower shrinkage [14] (1.2–4.0 % vs. 8.0 %, respectively). These features explain their very good adhesive properties [8] and resistance to environmental degradation agents [7].

Vinylester resins exhibit intermediate properties and cost with respect to polyester and epoxy resins. In particular, vinylester combines the improved performance of epoxy with the easier processing of polyester [14]. The better durability of vinylester compared to polyester explains why the majority of commercially available FRP bars used to reinforce concrete elements are made of a vinylester matrix [7]. Several FRP profiles are also available in vinylester resin for applications with particular durability requirements.

The main advantages of phenolic resins stem from their fire reaction behaviour: under elevated temperature or heat, they are much less flammable and produce less smoke than other thermosetting resins (see Chap. 5). In addition, phenolic resins are relatively economical, presenting a similar cost to polyester [7], have good dimensional stability and are able to keep their adhesive and mechanical properties at relatively high temperatures [8]. The main drawbacks are associated with the difficulty in reinforcing and curing phenolic resins which, in addition, present a brownish colour and are difficult to pigment [7].

Polymerization Agents

Polymerization agents are used in combination with the base resin to trigger its polymerization reaction. The curing reaction of polyester and vinylester resins is generally initiated with organic peroxides (activated by heat), used in quantities varying from 0.25 to 1.50 % (by weight of the resin). The polymerization of epoxy resins is initiated with curing agents (or hardeners) of the amine type, which are typically added at ratios of 25–50 % (also by weight of the resin) [7].

Fillers

Fillers are used in the polymeric matrix, on the one hand, to reduce the final costs of the FRP product and, on the other hand, to improve the performance with regard to certain properties, which would not be achieved if using only the resin and the fibres. As an example, fillers may allow obtaining a better fire performance by reducing the organic content of the matrix (this specific issue is discussed in detail in Chap. 5). Furthermore, fillers may also improve the dimensional stability of the matrix by reducing its shrinkage, thus avoiding the development of cracks in discontinuity zones or parts with excessive resin content. Cracking prevention may also increase the resistance to environmental degradation agents. Adding fillers to the matrix can improve several other properties, among which the hardness, the creep performance and the fatigue and chemical resistances [60].

The fillers most currently used with FRP products include calcium carbonate, cauline (aluminium silicate), alumina trihydrate and calcium sulphate. The two last compounds, in particular, are generally used to improve the fire behaviour of composite materials, by reducing their flammability and smoke production.

In non-structural FRP materials, the filler content may represent up to 40–65 % of the total weight of the matrix [14]. Nevertheless, in typical pultruded FRP profiles and FRP bars the filler content ranges from 10 to 30 % of the resin matrix weight. Small pultruded parts, comprising primarily unidirectional roving reinforcement, usually present even lower filler contents, less than 5 % by weight. FRP strips are generally not filled [7].

If some improvements can be obtained with the use of fillers, it must be stressed that the incorporation of fillers in the resin system usually decreases the key mechanical properties of FRP materials, as well as their durability performance [7].

Additives

Aiming at enhancing the material processing, improving the performance of the final product or simply modifying certain properties, it is possible to incorporate a wide variety of additives in the resin system. Additives are generally used to fulfil one of the following objectives [14]:

- Reduction of flammability and smoke production when submitted to fire (flame retardant additives)

- Inhibition of polymer oxidation (antioxidants)
- Reduction of shrinkage (low profile or shrink additives)
- Reduction of voids content
- Increase of electrical conductivity (by adding metal and/or carbon particles) and electromagnetic interference (adding conductive materials)
- Increase of toughness (rubber or other elastomeric materials)
- Reduction of the tendency to attract electrical charge (antistatic agents)
- Promotion of cellular structure (foaming agents), which reduces density, materials costs and shrinkage, improving, in addition, the electrical and thermal insulation
- Prevention of gloss loss, discolouration, cracking or disintegration due to UV radiation (UV stabilizers)
- Obtaining a certain colour (pigments or colorants)
- Facilitate removal from moulds (release agents)

Compared to fillers, additives are used in much smaller quantities, generally lower than 1 % of the matrix weight. However, in spite of those small quantities, and similarly to fillers, the physical and mechanical properties of the final FRP product may be considerably affected by the incorporation of additives in the matrix system.

11.3.2 Philosophy in the Development of FRP Composites

When developing FRP materials for civil engineering applications, one should bear in mind that their performance is influenced not only by the constituent materials (namely, the mechanical properties of the fibres and the matrix) and the composition and arrangement of the reinforcing fibres (namely, their type, orientation, length and stacking sequence), but also by the interaction between the fibres and the matrix, i.e. the fibre–matrix bonding. This interaction depends essentially on the adhesion and mechanical compatibility between the fibres and the matrix, and also on the angle between the fibres and the mechanical loading direction [47].

In such FRP product development, there is a wide range of alternatives through the combination of different base resins, additives and fillers to be used in the matrix, with various reinforcement (type of fibre, content, orientation, architecture), and by using different processing techniques.

The philosophy inherent to the development of FRP products has consisted in designing materials for specific requirements (such as lightness, chemical resistance, stiffness, strength), through a careful selection and arrangement of the constituent materials described in the preceding section. The wide range of FRP products available for different civil engineering structural applications, each one presenting specific in service performance requirements, were developed and manufactured using this *design approach*.

11.3.3 Manufacturing Processes

FRP composites used in civil engineering structural applications are generally manufactured by the following two techniques [7]: (1) pultrusion, in which FRP components are produced in a plant and then transported to the construction site, and (2) hand layup (or wet layup), in which FRP components are partially produced (impregnated) and cured on site. The pultrusion process is used to manufacture rebars (internal reinforcement), strips (external strengthening) and structural profiles. Hand layup is mainly used to apply FRP sheets on site (external strengthening).

11.3.3.1 Pultrusion

GFRP pultruded profiles are manufactured by pultrusion, which consists of an automated process of continuous production of parts with constant cross section. Pultrusion, which was first developed in the 1950s in the USA [7], allows producing profiles with open cross sections (such as I, H or U) or closed-form cross sections (tubular), as well as multicellular closed-form panels with internal webs. The total length of the pultruded elements is only limited by transportation requirements.

Pultrusion is a low-cost manufacturing process that allows converting directly the resin and the reinforcing fibres into a finished composite part. According to Zureick and Scott [66], among the different manufacturing processes of composite materials developed in the last four decades, pultrusion offers the best productivity/cost ratio.

In a general way, pultrusion can be considered to be divided in two phases. In a first phase, the fibre reinforcement, in its several forms (rovings, mats, surface veils), is impregnated by the liquid matrix. In a second phase, the matrix solidifies inside a heated mould, which has the shape of the cross section to be produced, therefore resulting a piece with predetermined shape and dimensions.

Figure 11.7 presents a scheme of the assembly line of GFRP pultruded profiles through traditional pultrusion, where it is possible to distinguish six key elements: (1) set of spools stacked on creels for fibre reinforcement handling, (2) preforming guides, (3) resin impregnation bath (or, in alternative, resin injection system), (4) forming and curing die, (5) pulling system and (6) cutting system.

Downstream the production line, the rovings and mats are dispensed from a set of spools, stacked on metal racks or creels (Fig. 11.8a), and are guided through preforming guides (Fig. 11.8b), which allow positioning the different reinforcement types according to a pre-established fibre architecture for each of the laminates that will constitute the pultruded part.

In the traditional pultrusion process, fibres are impregnated by the matrix in an open bath system (Fig. 11.8c) before entering the metallic mould, and the resin in excess is removed when fibres pass through preforming guides, as illustrated in Fig. 11.8d. In modern pultrusion machines, which are presently the most commonly used for large-scale production, there is not an open bath system. Instead, reinforcements enter dry into an injection chamber (which is frequently an integral part of the die), where they are impregnated with the polymeric matrix (resin with

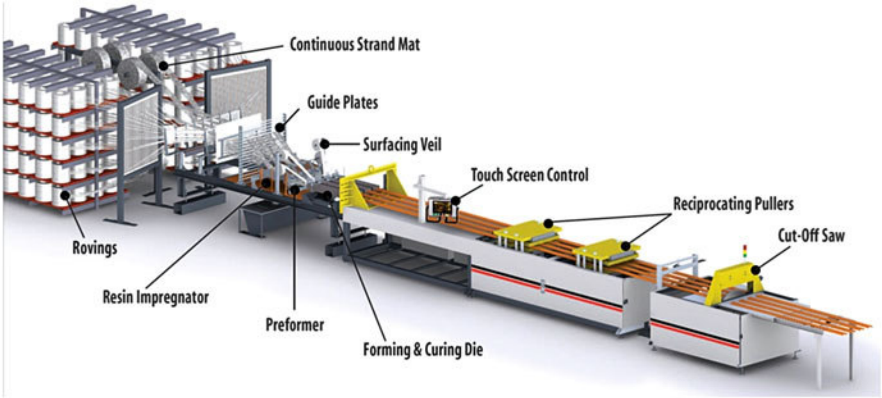

Fig. 11.7 Pultrusion assembly line (courtesy of Strongwell)

Fig. 11.8 Different stages of the pultrusion process: (**a**) creel and mat racks for fibre handling, (**b**) orifice plate, (**c**) open bath (courtesy of ALTO), (**d**) preforming guides, (**e**) cutting system (courtesy of Strongwell)

fillers and additives), supplied under pressure. This new resin injection system enables a more accurate control of the reinforcement position, providing higher material uniformity, and allows for a higher degree of fibre impregnation. Furthermore, during the manufacturing process, it also allows to introduce changes in the composition of the matrix more rapidly. Finally, resin injection reduces the evaporation of solvents from the matrix, thereby providing a healthier work environment than the open bath system.

Regardless of the impregnation process of the fibres, as the wet reinforcement travels through the heated die, typically in a length of 0.5–1.0 m, curing of the matrix takes place at temperatures varying from 90 to 180 °C, depending on the resin system used [7]. As a consequence of the curing process, the composite part shrinks and separates from the internal walls of the die, leaving the die as a finished product, with dimensional stability.

The cured part is then pulled by reciprocating pullers, synchronized to provide a constant speed. At the end of the assembly line, an automated and moving cut-off saw is used to obtain preset lengths of product, without stopping the manufacturing process (Fig. 11.8e).

The pultrusion rates of production greatly depend on the type of machine used and also on the shape of the cross section being produced. In average, a current cross section may be produced at a rate of 2 m/min [8].

11.3.3.2 Hand Layup

The hand layup method, probably the oldest in the composites industry, basically consists of applying successive layers of fibre reinforcement and its subsequent impregnation with a certain polymeric matrix, curing into a solid FRP component. This FRP composite will form into the shape and dimensions of the mould or surface in which it was produced.

This method, albeit simple, requires some specialization of the labour, as well as a certain level of quality control. Hand layup can be used with different complexity degrees in order to improve the quality of the finished product (in terms of volume and position of the fibres and volume of voids). As an example, the curing degree of the different layers can be improved by means of elevated temperature, pressure and vacuum.

Hand layup can be applied in a plant or on site. When the manufacturing is made in a plant, FRP elements are produced inside a mould (that can be opened or closed), being removed after curing (for which release agents can be used). This process can be used, for instance, in the production of FRP sandwich panels.[3] In most construction industry applications, on-site manufacturing is used, in which FRP elements are directly applied over the surface of an existing structural element that is intended to be strengthened (Sect. 11.6.5). Here, the main difficulty or concern consists of guaranteeing an adequate connection between the FRP element and the structural element to be strengthened. In this regard, in addition to a proper surface preparation, the success of the strengthening procedure relies on the adequate selection of the fibres and the resin.

In most civil engineering structural applications, the hand layup technique is used in its most elementary form, i.e. without application of external pressure, with the curing process taking place at ambient temperature. On the other hand, in the vast majority of applications, epoxy resins are used together with carbon or glass reinforcing fibres.

11.3.3.3 Other Processes

Besides the two aforementioned processes, used in the vast majority of civil engineering structural applications, there are other manufacturing processes, mainly used in the industrial production of individual components, namely the following:[4] (1) filament winding, used in the production of tubular elements; (2) centrifugation; (3) resin transfer moulding (RTM); (4) resin infusion moulding (RIM); and (5) vacuum-assisted resin transfer moulding (VARTM), the three latter being used in the production of panels for bridge decks and jackets for columns strengthening.

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[3] In composite sandwich panels, the FRP skins provide the axial/bending stiffness and strength. The core (often made of rigid foam or cellular plastic), with much lower density and mechanical performance, provides shear stiffness and strength, as well as thermal insulation.

[4] These production techniques, less frequent in FRP products used in the construction industry, are described in detail in [8].

11.3.4 Field of Application of FRP Materials in Civil Construction

FRP materials have been used in civil engineering applications basically in two forms: as tensile components (strips, sheets, bars or cables) or as bending components (profiles, cellular or sandwich slab panels), according to their one-dimensional or two-dimensional structural action, respectively [45].

In general, the following four basic fields of application of FRP materials in civil engineering can be identified [45]: (1) FRP rebars for internal reinforcement, (2) repair and strengthening[5] (usually external), (3) new hybrid structures and (4) all-FRP new structures.

GFRP pultruded profiles, whose general characterization is presented in Sect. 11.4, are included essentially in the last two fields of application, although they can also be used in repair and strengthening of existing structures. FRP rebars, described in detail in Sect. 11.5, are mainly used as internal reinforcement of concrete structural elements, whereas FRP strips and sheets, presented in Sect. 11.6, are typically used in the repair and strengthening of existing structures.

11.3.4.1 Rebars for Internal Reinforcement of New Structures

In this field of application, steel reinforcing bars are partially or fully replaced by short fibres (glass reinforced concrete (GRC[6]), which has been used in several applications, among which façade panels and telecommunication towers [28]), textiles and FRP bars or internal prestress cables. Regarding the last type of reinforcement, several concrete bridge decks located in aggressive environments have been reinforced using exclusively GFRP bars (Fig. 11.9), due to their corrosion resistance[7] and relatively competitive cost. This type of rebars has also been used in retention walls, tunnelling and masonry repair. Although much less frequent, it is worth mentioning the possibility of using CFRP bars and prestress cables as internal reinforcement of bridge decks.

11.3.4.2 Repair and Strengthening of Existing Structures

In this field of application, strips, sheets, bars and external prestress cables (Fig. 11.10) have been used to repair and strengthen existing structures, especially made of reinforced concrete. Of particular importance is the use of CFRP strips (Fig. 11.11)

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[5] Repair and strengthening are two types of rehabilitation interventions on existing structures. In the case of repair, the objective is to increase the strength, stiffness or ductility of the structure up to the original levels it was designed for. This operation may be needed due to design and/or construction errors, or when the original structure degraded due to environmental effects or service conditions. In the case of strengthening, the objective is not to reinstall the original capacity but rather to upgrade the structural performance compared to the original design. This operation may be justified by several reasons, namely, the need to comply with new (stricter) regulation and/or changes in the service conditions.

[6] Strictly, GRC is not an FRP material as it features a cementitious matrix.

[7] The use of GFRP bars in bridge decks where de-icing salts are commonly used during winter and which are further expected to resist to freeze-thaw cycles can be particularly advantageous.

Fig. 11.9 Concrete bridge deck reinforced with GFRP bars

Fig. 11.10 CFRP cables used in external prestressing of Verdasio Bridge [46]

Fig. 11.11 CFRP laminates used in the strengthening of *Duarte Pacheco* Viaduct

Fig. 11.12 CFRP sheets used in the strengthening of *Duarte Pache*co Viaduct

and sheets (Fig. 11.12), which have been applied essentially to strengthen decks and columns of bridges. These solutions have already undergone the period of pilot applications and constitute already well-established techniques, which have presented a very significant rise in the second half of the 1990s [45].

11.3.4.3 New Hybrid Structures

In this case, FRP materials have been used in combination with traditional materials or have replaced them in certain components of new structures, such as external cables, girders or even slabs, especially in bridge decks. In most of this type of applications, the full potential of FRP materials is not always exploited, particularly when the design is more oriented towards the use of the traditional material [46]. Several bridges have been built using external FRP cables, and, moreover, several pedestrian and vehicular bridges have already been erected with FRP decks (Fig. 11.13).

11.3.4.4 All-FRP Structures

In this type of application, structures are built exclusively with FRP materials. The design of some of these new structures often incorporates material-adapted concepts, allowing for a better exploitation of the FRP materials potential. In bridge construction, these structural applications correspond essentially to the decks, since piers and abutments are still being constructed using traditional materials. One of the most emblematic examples of such applications is the Pontresina Bridge (Fig. 11.14), in Switzerland, whose superstructure consists of two lateral trusses made of GFRP profiles and a deck also made of GFRP panels.

In addition to the above-mentioned primary structural applications, FRP materials have also been used in secondary structures or nonstructural elements of constructions. Among these secondary applications, some of which are described in further detail in Sect. 11.4, are ladders, handrails and parapets, working platforms and walkways, flooring planks and façade panels.

Fig. 11.13 Steel/GFRP hybrid footbridge in Viseu, Portugal

Fig. 11.14 All-FRP Pontresina footbridge [46]

11.3.5 Durability of FRP Materials

Comparing with traditional materials, there is practical evidence of improved performance of FRP composites when submitted to aggressive environments. This can be perceived by the long history of their use in marine vessels, piping, storage tanks and in several corrosive applications, such as oil, chemical and water treatment industries.

For civil engineering structural applications, the previously described Pontresina Bridge (see Sect. 11.3.4.4) stands as an example of such evidence. After 8 years of use, the bridge was subjected to a detailed assessment that included a visual inspection, investigations of material degradation, full-scale load testing and mechanical tests on cut-outs [42]. Visual inspection evidenced the occurrence of local defects and damage that included local crushing caused by impacts during movement of the bridge, local cracks due to inappropriate storage and lifting, fibre blooming due to misalignment of the surface veils, a slight yellowing of the material and also damages due to vandalism. The authors attributed most of the damage to inappropriate manufacturing and constructive detailing, namely, the choice of open cross sections with thin free flanges, acknowledging that closed cross sections (such as hollow members) would have been far less sensitive to such actions. Load tests showed that the structural safety and serviceability of the bridge was not significantly affected.

Paradoxically, in spite of such practical evidence of improved durability, one of the factors that is delaying the widespread acceptance of GFRP pultruded profiles in the construction industry as load-carrying structural elements is the lack of comprehensive and validated data on durability [48], which creates an obstacle for the construction agents (including owners, designers and contractors), as civil infrastructure service life is generally expected to exceed 50 years.

Durability has been recently identified by several authors as the most critical gap between perceived need of information and available information, regarding future research [48, 36], particularly for composites produced by large-scale processing methods, such as pultrusion. Kharbari et al. [49] identified the following environmental conditions as those that influence more significantly the durability of FRP materials used in civil engineering applications, all requiring additional research in the future: (1) moisture/solution, (2) thermal effects, (3) ultraviolet radiation, (4) alkalinity, (5) creep/relaxation, (6) fatigue and (7) fire.

Several studies were carried out since the late 1980s to investigate the effects of those environmental conditions on the properties of FRP materials used in civil engineering applications, in terms of magnitude and mechanisms of degradation. Reviews of those investigations (presented in [48, 49, 57, 50]) indicate that test methods used in those studies can vary considerably (standardized test methods do not exist yet), most investigations were performed under accelerated conditions for maximum durations that rarely are superior to 18 months, very few studies analysed the combined effect of mechanical loading and environmental degradation and, finally, several contradictory results were published within those studies [47, 48].

The practical applications and scientific studies conducted so far have attested the overall good performance of FRP materials when subjected to aggressive environments, particularly when compared with traditional materials [22]. In order to guarantee a good performance, the key element seems to be the adequacy of the polymeric matrix to the environmental aggressiveness—in harsher environments, as an alternative to the most conventional polyester resin, it is generally preferable to adopt resins with improved behaviour, such as vinylester or even epoxy.

11.3.6 Sustainability of FRP Materials

The sustainability of all construction materials has to be assessed taking into account the various phases of their life cycle, namely the following: (1) the manufacturing phase, (2) the service life and (3) the end of the life cycle.

First of all, for the manufacturing phase, one must consider the collection of the raw materials, the energy required for industrial production and the waste produced at this stage. Subsequently, for the service life phase, the durability (high for FRP), the maintenance requirements (low for FRP) and the energy consumption have to be taken into account. Finally, at the end of the life cycle, the various waste management options (in decreasing order of preference, reuse, recycling, incineration and landfill) need to be considered.

When assessing the production phase, in terms of raw materials, glass fibres result from quartz powder and limestone, which are largely available resources [47], and an important fraction of the raw material comprises recycled glass. Regarding polymeric resins, they result from fossil resources; however, the resins used in FRP materials are generally by-products of the oil industry; furthermore, even if the use of FRP materials would increase drastically, the raw materials demand would still be negligible compared to the total consumption of fossil fuels. In terms of energy requirements, it should be noted that GFRP profiles consume only 1/6 and 1/4 of the energy needed to produce aluminium and steel, respectively [47]. Advanced composites made of carbon fibres involve much higher energy consumption, due to the large quantity of energy involved in the production of those fibres.

During service life, FRP materials offer some advantages compared with most traditional materials (namely, steel, reinforced concrete and timber), as they require limited maintenance and, as previously discussed in Sect. 11.3.5, they present improved durability even when applied in chemically aggressive environments. In addition, the low thermal conductivity of the material may provide energy savings when used in building applications (this advantage is attested by the *Eyecatcher Building*).

The most important limitation of FRP materials in terms of sustainability takes place at the end of the life cycle. In fact, due to non-reprocessability of thermosetting resins (as mentioned, the most common for civil engineering structural applications) there are relatively limited waste management alternatives. As previously referred, once polymerized, these resins can no longer be reprocessed. As a consequence, presently, at the end of the service life, the most frequent waste management option involves processing the FRP materials to granulates and using them as landfill material, which has limited intrinsic value.

The volume of FRP waste produced during the production phase (typically resulting from trial runs, trimming dust and defective items) and building site operations (generally off-cuts) is very low [19]. The vast majority of FRP waste results from deconstruction or end of service life. The present volumes of FRP waste are still negligible when compared to other forms of material.[8] However, the future volumes of FRP waste are expected to increase and impending European legislation on construction and demolition waste will increase landfill taxes, therefore stimulating reuse and recycling and strongly discouraging disposal.[9]

Because FRP materials are often made to order, being usually designed for a particular application [19] and not meeting standardized material properties or shapes, the practical possibilities of reuse (a highly rated solution in the waste

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[8] According to Pickering [54], approximately one million tonnes of composites are manufactured each year in Europe.

[9] In several European Union countries (e.g. Germany), it is already illegal to landfill composites waste [54].

hierarchy) are presently very limited. With particular regard to GFRP pultruded shapes, their reuse seems quite implausible, due to the difficulties in determining the residual mechanical properties or in reliably assessing material degradation or viscoelastic effects [19].

Due to the non-reprocessability of thermosetting resins, various technologies have been developed in order to recycle thermoset FRP composites. These techniques, comprehensively reviewed by Pickering [54], can be divided in two groups: (1) mechanical recycling, which involve mechanical comminution techniques to reduce the size of the scrap to produce recyclates and (2) thermal recycling techniques, that use thermal processes to break the scrap down into material and energy (fibre recovery techniques, burning in cement kilns or simple material incineration).

The following applications involving the use of recyclates (obtained from mechanical recycling) were recently investigated: incorporation in thermoplastic matrixes; substitution of filler in new thermoset compounds; manufacturing of plastic lumber; reinforcement of wood particle boards; and production of road asphalt and concrete [19, 54]. If the incorporation of recyclates in such applications may offer technical advantages, the prospects for commercial operation are still to be achieved. With this regard, the main limitations are the scarce throughput supply, the price of the recyclates and the absence of developed markets [54].

In the future, it is possible that FRP materials become at least as sustainable as the traditional construction materials they compete with (concrete, steel) [47]. This depends on the success of the development of thermoplastic resins. Besides being reprocessable, after recycling these resins keep the vast majority of their original mechanical properties [63].

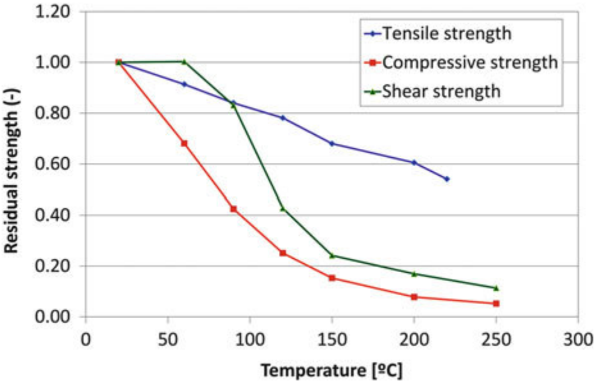
11.3.7 Fire Behaviour of FRP Materials

Construction materials used in buildings are required to have adequate fire reaction behaviour, avoiding fire deflagration, flame spread and excessive smoke production and spreading. Additionally, structural elements are also required to have sufficient fire resistance, in order to prevent structural collapse under fire during a sufficient period of time, thus allowing the safe evacuation of users.

In this context, there are legitimate concerns with the fire behaviour of FRP materials, which have hindered the widespread use of these composite materials in structural applications, particularly in buildings. In fact, when FRP materials are exposed to high temperatures (300–500 °C), their organic matrix decomposes, releasing heat, smoke, soot and toxic volatiles. Also when heated to moderate temperatures (100–200 °C), FRP materials soften, creep and distort; therefore, the mechanical properties suffer remarkable reductions, particularly those that are more matrix dependent (Fig. 11.15).

In spite of these unfavourable properties, FRP materials present other attributes that are useful in a fire situation. In opposition to other traditional materials, such as steel, composites are very good heat insulators, and this feature is important for

Fig. 11.15 Residual tensile, compressive and shear strengths as a function of temperature [23]



slowing the spread of fire from room to room. Also when compared to steel, composites present better burn-through resistance, providing an effective barrier against flame, heat, smoke and toxic fumes. Furthermore, several measures, both passive and active, can be applied to improve the fire performance of FRP materials [24, 20, 21].

11.4 GFRP Pultruded Profiles

11.4.1 Structural Shapes of GFRP Pultruded Profiles

The first structural shapes of GFRP pultruded profiles basically mimicked those from metallic construction, generally exhibiting thin-walled open or tubular cross-sections. The most frequent cross-sections of the so-called first-generation profiles are illustrated in Fig. 11.16.

The typical fibre architecture of the laminates (webs or flanges) of GFRP pultruded profiles is schematically illustrated in Fig. 11.17. Those laminates are constituted by alternating layers of rovings, comprising reinforcement in the axial direction, and mats, with fibres oriented in various directions, therefore contributing to the mechanical performance in the transverse direction and also under shear loading. In general, the outermost layer of the laminates comprises a surface veil, consisting of a thin chopped strand mat, with short and randomly oriented fibres. This superficial layer creates a smooth surface finish and provides additional protection against the environmental agents due to its increased resin content.

The above-mentioned first-generation GFRP pultruded profiles are presently used in most structural applications. However, they exhibit several disadvantages that generally stem from their susceptibility to compressive and impact loads. In fact, in most applications, the resistant capacity of the material is seldom reached because the flanges of beams and the flanges/webs of columns often buckle well before material failure. This points out the need of developing material-adapted pultruded forms in order to allow for a better use of the GFRP material.

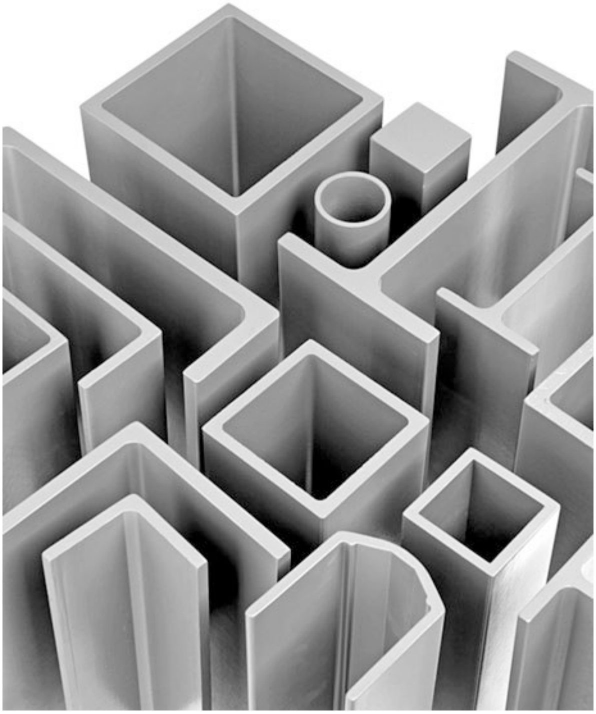


Fig. 11.16 Typical shapes of first-generation profiles (courtesy of Fiberline)

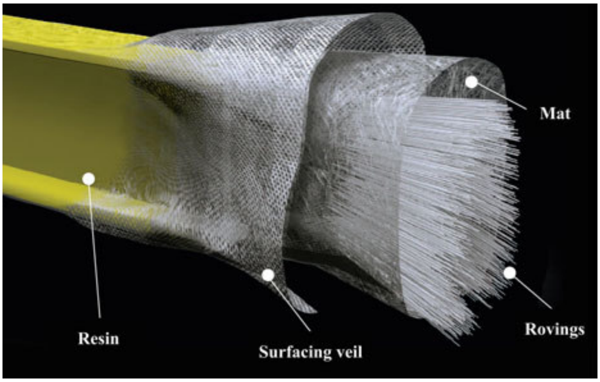


Fig. 11.17 Typical fibre architecture of the laminates of pultruded profiles (courtesy of Strongwell)

The use of a new structural material with the same shapes as the traditional materials that the former intend to replace is not a new trend in the history of construction. According to Keller [44], prior to the development of material-adapted forms, adapted to the specific properties of a new material, there is typically a substitution phase. Stone started to be used replacing timber entablature in Egyptian temples 5,000 years ago, but the stone arches, which actually constitute

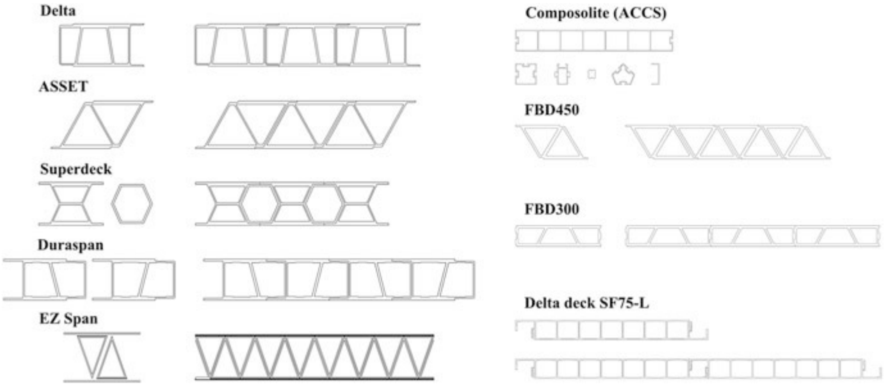


Fig. 11.18 Pultruded bridge deck systems (adapted from [45])

the material-adapted form, were developed much later, and their industrialized use occurred only with the Romans, after the invention of the corbel. Similarly, about 200 years ago, the arches of the first iron bridges were built reproducing the same construction technologies used to erect stone arches, and the first iron trusses and frames were developed only more than 80 years later. Also with concrete, about 100 years ago, it was used essentially in linear structural elements, mimicking steel frames, and it was not before 40 years that the more material-adapted forms were developed, when concrete started to be used in laminar elements.

According to Keller [44], there are two main reasons for this historical regularity in what concerns the use of new construction materials and the evolution of their structural forms. On the one hand, when a new material is introduced, the adapted material forms are simply not known—thus, there is a technical or scientific reason for a substitution phase. On the other hand, by copying the structural form of the material which is intended to be replaced, a better acceptance is guaranteed for the new material—therefore, in addition, there is a confidence or commercial reason for such substitution phase.

More recently, several composites manufacturing companies started to develop new structural shapes, better adapted to the specific properties of FRP materials. These new structural systems, which have been used mostly in the new construction or replacement of bridge decks, essentially consist of multicellular pultruded panels (Fig. 11.18) that are connected to each other through adhesive bonding or snap-fitting, constituting slab elements of constant thickness. Because they are significantly lighter than traditional bridge decks, these new deck systems allow for substantial savings in column and foundation works and enable higher live load levels.

Table 11.3 Typical mechanical properties of GFRP pultruded profiles (adapted from [47, 7, 31, 25])

Property	Test standard	Axial direction	Transverse direction
Tensile strength [MPa]	ISO 527, ASTM D 638	200–400	50–60
Compressive strength [MPa]	ISO 14126, ASTM D 695	200–400	70–140
Shear strength [MPa]	ISO 14129, ASTM D 3846	25–30	
Elasticity modulus [GPa]	ISO 527, EN 13706-2	20–40	5–9
Shear modulus [GPa]	ISO 14129, EN 13706-2	3–4	

11.4.2 Typical Properties of GFRP Pultruded Profiles

As for most FRP materials, the properties of GFRP pultruded profiles depend to a great extend on the characteristics of their constituent materials (type of fibres and polymeric matrix), on the fibre content and architecture and also on the fibre–matrix interaction.[10]

Taking into consideration the numerous possibilities of combining those elements, together with the fact that the GFRP pultruded profiles commercialized by the main manufacturers are not standardized, it is only possible to refer typical ranges of variation for their mechanical properties. Table 11.3 lists the usual variation ranges for the most important mechanical properties of GFRP profiles produced by some of the biggest manufacturers.[11] It should be noted that given the previously shown internal constitution of the laminates, the material presents an anisotropic behaviour, with higher mechanical properties in the axial pultrusion direction, along which rovings are aligned, than in any other direction.

Figure 11.19 presents the tensile strength and the elasticity modulus in bending, both in the longitudinal direction, of GFRP pultruded profiles produced by a European manufacturer. In the same figure, a comparison is made with typical values of those properties presented by other materials, namely, PVC, aluminium, steel (class S360) and timber (spruce specie). Among these materials, steel is the one that competes most directly with GFRP pultruded profiles.

Figure 11.19 shows that the tensile strength of GFRP profiles in the axial direction is similar to that of most structural steel grades. However, the following main differences are outlined: (1) the linear elastic stress–strain relationship until failure of GFRP profiles, which contrasts with the ductile behaviour of steel, and (2) the relatively low elasticity modulus of GFRP profiles, about 15–20 % of steel.

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[10] Additionally, the response of FRP materials depends on external factors, such as the loading regime and the exposition environment (temperature, moisture).

[11] According to Bank [7], these properties are often based on coupon testing and can be assumed to be the lower bounds for the class of profiles indicated in the manufacturers' manuals. Unfortunately, no additional data are presently provided to determine the statistics of those properties, which are needed to perform probability-based design.

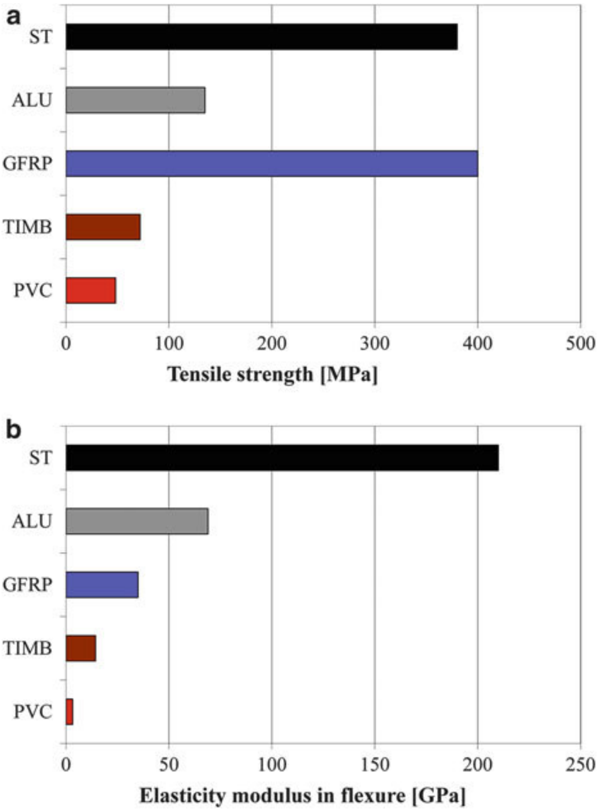

Fig. 11.19 Comparison between mechanical properties of GFRP profiles and steel (ST), aluminium (ALU); timber (TIMB) and PVC: (**a**) tensile strength and (**b**) elasticity modulus in flexure (adapted from [31])

Table 11.4 Physical properties of GFRP pultruded profiles (adapted from [47, 31, 25])

Property	Test standard	Axial direction	Transverse direction
Density [g/cm^3]	ISO 1183, ASTM D 792	1.5–2.0	
Fibre content [%]	ISO 1172, ASTM D 3171	50–70	
Thermal expansion coefficient [K^{-1}]	ISO 11359-2, ASTM D 696	8–14 × 10^{-6}	16–22 × 10^{-6}
Thermal conductivity [W/K.m]	ISO 22007, ASTM D 5930	0.20–0.58	

The relatively low elasticity modulus is associated with an increased deformability of the structures, for which the shear deformation may also give an important contribution, especially in non-slender elements. Actually, the design of GFRP pultruded profiles is often driven by serviceability requirements rather than by strength limitations. Furthermore, the low elasticity modulus is also responsible for an increased susceptibility to instability phenomena in slender members.

Fig. 11.20 Comparison between physical properties of GFRP profiles and steel (ST), aluminium (ALU); timber (TIMB) and PVC: (**a**) density, (**b**) thermal expansion coefficient and (**c**) thermal conductivity (adapted from [31])

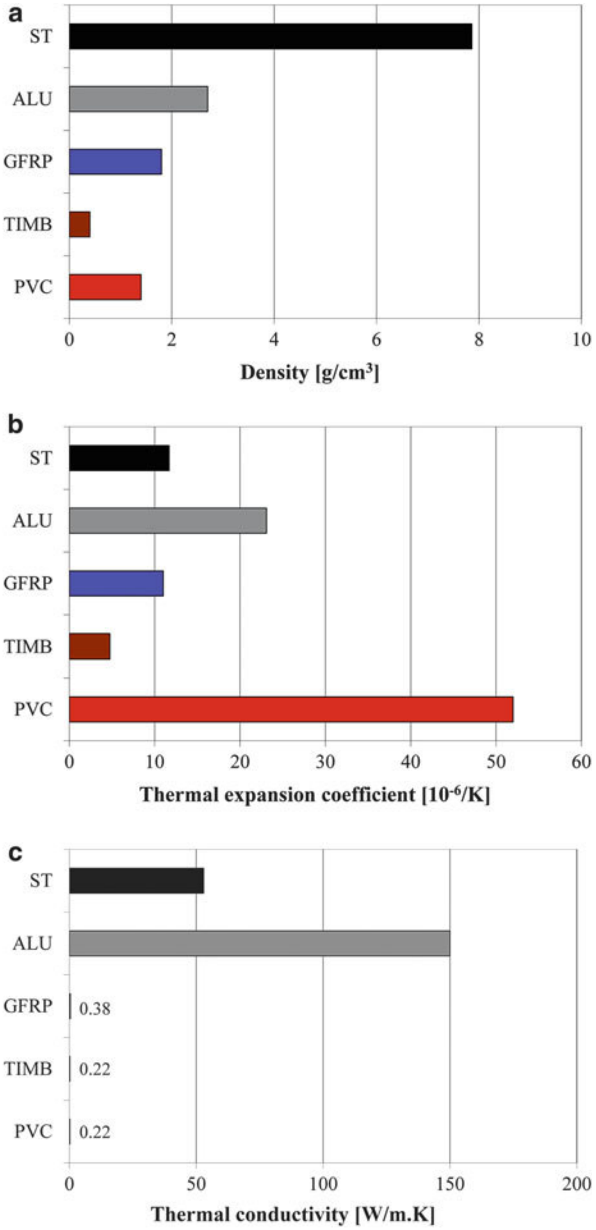

Table 11.4 presents the typical variation ranges of some physical and thermal properties of GFRP pultruded profiles produced by some of the biggest manufacturers.

Figure 11.20 presents a comparison between the density (ρ), the thermal expansion coefficient (α) and the thermal conductivity (λ) of GFRP pultruded profiles and the corresponding values of other materials, namely, PVC, timber, aluminium and steel.

From Fig. 11.20 the following properties of GFRP pultruded profiles are outlined and compared to those of steel: reduced self-weight, about four to five times less than that of steel, thermal expansion coefficient similar to steel and very low thermal conductivity coefficient, significantly lower than that of steel.

11.4.3 Advantages and Difficulties in the Use of GFRP Pultruded Profiles

When compared to traditional materials, such as steel or reinforced concrete, GFRP pultruded profiles present the following advantages:

- Low self-weight
- High strength-to-weight and stiffness-to-weight ratios
- Possibility of producing any cross section
- High fatigue strength
- Thermal insulation and electromagnetic transparency
- Easy transportation to the construction site and application
- Low maintenance costs
- High corrosion resistance and long-term durability

However, and again comparing to traditional materials, the following difficulties or limitations have to be faced when using GFRP pultruded profiles as structural elements:

- Low elasticity modulus, which causes structural members to present considerable deformability and susceptibility to instability phenomena (either local or global), which may prevent the full exploitation of the material properties
- Fragile behaviour, in contrast with the design philosophy subjacent to most design codes and also with the current design practice
- Need to develop new material-adapted structural forms, for both all-composite and hybrid applications (in combination with other materials), as well as material-adapted connection technologies
- Fire behaviour, which often requires protective measures, due to the flammability, the heat and smoke release and, more importantly for structural applications, the loss of mechanical properties for relatively low temperatures
- Lack of specific design codes, with most structural designs being based on manufacturers' design guides
- Initial costs, which are still not very competitive in most applications, moreover, when most owners do not make their decisions based on life-cycle costs, for which GFRP pultruded profiles would allow for important savings when compared to traditional materials

Fig. 11.21 Examples of GFRP pultruded products for nonstructural applications and secondary structures: (**a**) insulated ladders, (**b**) stairways with handrails, (**c**) floor gratings, (**d**) working platforms and walkways, (**e**) building façade panels (courtesy of Strongwell)

11.4.4 Field of Application of GFRP Pultruded Profiles

The first applications of GFRP pultruded profiles essentially included non-structural elements or secondary structures with specific requirements in terms of lightness, durability in harsh environments or electromagnetic transparency, not possible to fulfil with traditional materials. The above-mentioned features of GFRP were the key factor for the adoption of pultruded profiles in various fields of application, which included basic sanitation, water and waste treatment plants, petrochemical industry, thermo-electrical plants, railway transportation, fishing industry and navigation ports.

The pultrusion industry has developed a wide range of GFRP pultruded products for non-structural elements or secondary structures that include garden benches, cable pathways, doors and gates, insulated ladders with cages (Fig. 11.21a), banisters, stairways with handrails (Fig. 11.21b), gratings and plank systems for flooring (Fig. 11.21c), working platforms and walkways (Fig. 11.21d) and building façade panels (Fig. 11.21e).

Despite the fact that applications in non-structural elements or in secondary structures are still much more numerous, in the last years, important applications of GFRP pultruded profiles in primary structures started also to be developed. Initially driven forward in the scope of pilot and/or research projects, these applications are now finding their own way, concerning pedestrian and vehicular bridges and, less frequently, buildings.

Fig. 11.22 The *Aberfeldy* bridge [13]

Fig. 11.23 The *Bonds Mill* Lift Bridge [13]

11.4.4.1 Examples in New Construction

The first all-composite pedestrian bridge was built in the UK in 1992. The 131 m long cable-stayed *Aberfeldy* bridge (Fig. 11.22) has a deck constituted by ACCS panels (cf. Fig. 11.18), suspended from GFRP towers by aramid cables.

The lightweight of GFRP pultruded profiles was also exploited in the construction of the Bonds Mill Lift Bridge (Fig. 11.23), the first all-composite vehicular bridge, constructed in the UK in 1994. The bridge deck was also built using ACCS panels, supported by longitudinal girders made of GFRP pultruded profiles [13]. In bascule bridges, the lightweight of the decks constitutes an obvious advantage, allowing for very significant savings in the mechanical elevation systems.

In 1997, an emblematic two-span bridge was constructed in Pontresina, Switzerland, constituted by two 12.5 m long lateral trusses using only GFRP pultruded profiles (Fig. 11.24a). In one span, all joints were made by bolting, while in the other span, adhesively bonded connections were used for the first time [46]; all connections were prefabricated in a workshop with consequent advantages in terms of economy and quality control. The pedestrian bridge was

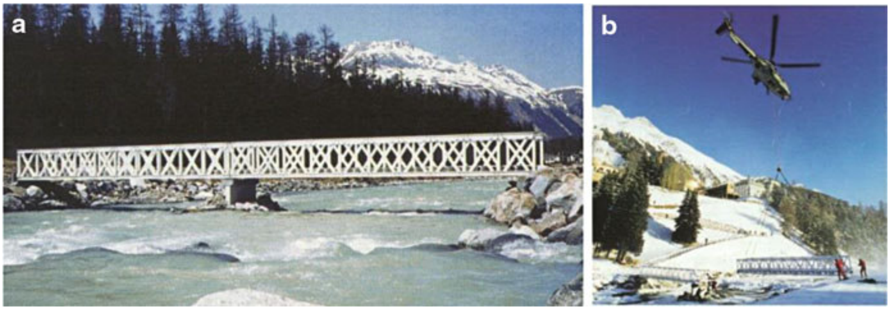

Fig. 11.24 The *Pontresina* bridge: (**a**) general view and (**b**) installation of a span [46]

Fig. 11.25 The *Kolding* bridge: (**a**) general view, (**b**) transport of a 27 m long bridge segment and (**c**) bridge installation during the night [12]

designed in order to be removed each year at the end of winter, before snow melts, and reinstalled again once the flooding risk has passed. Therefore, lightweight was a critical factor for the selection of GFRP pultruded profiles. Installation was carried out in only 4 h, in a process which involved lifting the two spans with a helicopter, as shown in Fig. 11.24b. Another decisive factor for material selection was the improved corrosion resistance of the GFRP pultruded profiles [44].

Also in 1997, the pedestrian *Kolding* bridge was built in Denmark, which was the first all-composite bridge to be constructed in Scandinavia and the first composite bridge worldwide to cross a railway line. The cable-stayed bridge has two spans of 27 and 13 m, supported by a central pylon (Fig. 11.25a). All structural elements, including the stays, were built using only GFRP profiles, and, as a consequence, there is no electromagnetic interference with the railway electrification. All connections were made on a workshop, and bridge erection was carried out in only 18 h (three nocturnal sessions limited to 8 h), without having to interrupt the railway circulation (Fig. 11.25b, c). The total weight of the bridge (12.5 tonne) is only less than half of the corresponding steel structure. Furthermore, the total initial costs were estimated to be only 5–10 % higher than those corresponding to the alternative steel or reinforced concrete solutions [12], while long-term costs are expected to be considerably lower.

Fig. 11.26 The *Lleida* bridge: (**a**) general view (courtesy of Juan Sobrino/PEDELTA) and (**b**) lateral view [59]

The *Lleida* bridge, in Spain, was built in 2001, crossing three important transportation corridors: a roadway, a railway line and the new projected high-speed railway line between Madrid and Barcelona (Fig. 11.26a). Thus, the requirements for this pedestrian bridge were minimum maintenance, easy and quick erection and no electromagnetic interference with the railway electrification. The structure of the 38 m span bridge consists of a double-tied arch, with a rise of 6.2 m and a width of 3.0 m (Fig. 11.26b). All structural elements were made using only GFRP pultruded profiles, and all connections were bolted using stainless steel brackets and bolts. The total weight of the bridge (19 tonne) enabled erecting and installing the bridge in only 3 h [59].

The *Eyecatcher* building (Fig. 11.27a) was constructed in 1999 at the Swiss Building Fair, in Basel, and constitutes a milestone regarding the use of FRP materials in building construction. It consists of a five-storey building, the tallest ever erected, whose structure is constituted by three trapezoidal frames made of adhesively bonded built-up sections of GFRP pultruded profiles (Fig. 11.27b). The reduced self-weight of the material enabled the pre-assembly of most connections in a workshop, and, as a consequence, the on-site mounting of the main structure was carried out in only 3 days. The façade was constructed using sandwich panels with a total thickness of 50 mm (two glass fibre-reinforced polyester external skins with an insulating core), which provided simultaneous thermal and acoustic insulation. The low thermal conductivity of the GFRP pultruded profiles was also a decisive factor in material selection, in particular, the non-development of thermal bridges, which allowed a direct integration of the structural elements in the façade [44]. After the exhibition, the construction was disassembled and rebuilt at another location, also in Basel, where it is now serving as an office building [44].

11.4.4.2 Examples in Rehabilitation

All the previously shown examples of application concerned the use of GFRP pultruded profiles in new construction, of both bridges and buildings. In addition to these applications, GFRP pultruded profiles have also been used in the rehabilitation of degraded constructions.

Several degraded bridge decks were already replaced using the different deck systems shown in Fig. 11.18. In these solutions, the FRP bridge deck is typically

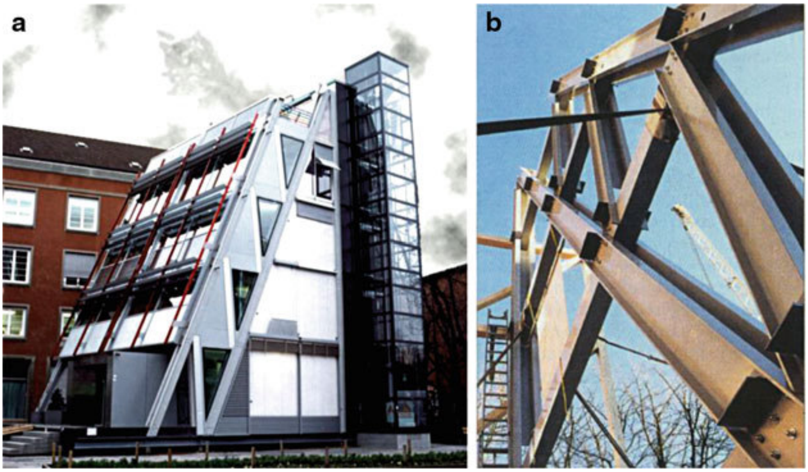

Fig. 11.27 The Eyecatcher building: (**a**) general view (courtesy of Thomas Keller) and (**b**) installation of one of the main frames [44]

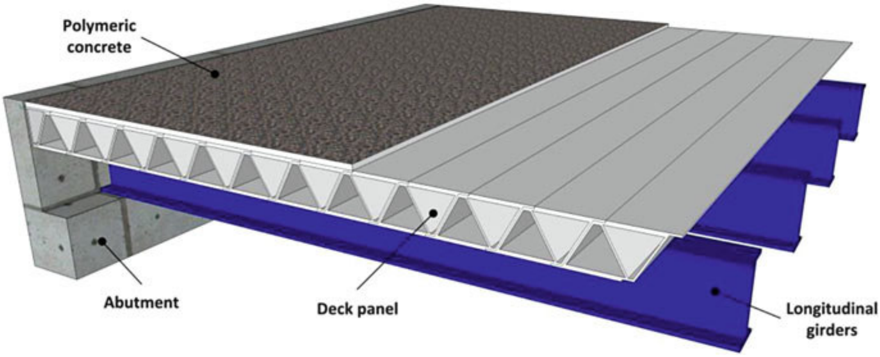

Fig. 11.28 Scheme of the ASSET bridge deck system (adapted from [38])

Fig. 11.29 Installation of Superdeck bridge deck (courtesy of Creative Pultrusions)

Fig. 11.30 Use of GFRP pultruded profiles in the rehabilitation of a degraded timber floor [32]

connected to supporting longitudinal girders by means of bolting, bonding or doweling, as illustrated in Figs. 11.28 and 11.29. These types of decks have very reduced self-weight (about 20 % of a comparable concrete deck [45]), improved durability and fatigue strength, easy maintenance and allow for very short installation times, requiring minimum traffic interruption.

Another field of application where the use of GFRP pultruded shapes (using either profiles or deck systems) seems to have a great potential is the replacement of degraded timber pavements of buildings located in old districts. In this specific application, the use of traditional solutions, with steel profiles or reinforced concrete elements, is most often either not possible, due to accessibility limitations (usually it is not possible to install a crane or other elevation devices), or at least very disadvantageous, due to the constraints associated with the additional self-weight introduced on the existing elements of the construction.

The intervention performed in the *Wörlitz* Castle, Germany, illustrates quite well the potential of using GFRP pultruded shapes in such applications. The load-carrying heavy timber beams that constituted the pavements of the castle had begun to rot at critical places, jeopardizing invaluable stucco ceilings and ceiling paintings of the late seventeenth century. To prevent the ceilings from falling down, it was decided to replace the degraded parts of the timber beams using GFRP pultruded profiles, which were bonded/bolted to the sound parts of the existing timber beams (Fig. 11.30). This rehabilitation solution proved to be extremely advantageous, not needing heavy weight lifting gear, introducing a negligible self-weight increase and, not less importantly, avoiding thermal bridges in the wall junctions.

11.4.5 Connections Between GFRP Pultruded Profiles

Connections between GFRP pultruded profiles are inevitable because shape sizes are limited by production constraints and there are also size limitations related with transportation and handling operations.

Connections between GFRP structural elements can be organized in the following types: (1) bolted, (2) bonded, (3) mixed (bolted and bonded), (4) interlocking

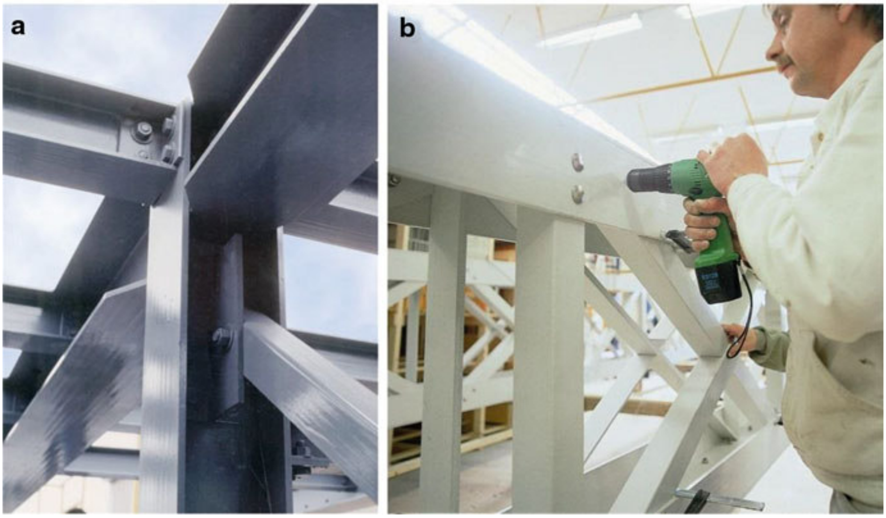

Fig. 11.31 Bolted connections between GFRP profiles of (**a**) three-dimensional frame (courtesy of Strongwell) and (**b**) pedestrian bridge (courtesy of Fiberline Composites)

and (5) welded. The most common techniques for joining structural FRP elements are mechanical fastening, adhesive bonding and the combination thereof [65].

The current practice of bolting FRP structural elements basically mimics the constructive details of metallic construction (Fig. 11.31). In most cases, this direct technology transfer (in line with the copy of structural steel cross-sections by first-generation profiles) leads to oversized FRP components, because it does not take into account the remarkable differences in the behaviour between FRP and steel. First of all, due to the anisotropic behaviour of FRP, transverse stresses inevitably develop in the joints causing constraints due to the lower material strength in such directions. In addition, because FRP presents linear-elastic behaviour and exhibits no plastic deformations, the stress concentrations in the vicinity of the bolt holes are higher compared to those observed in (ductile) steel. Due to the afore-mentioned differences between FRP and steel, at the design stage, the capacity of bolted connections very often governs the selection of the FRP pultruded cross-section.

Compared to bolting, adhesive bonding has been found to be much more adapted to the brittle and anisotropic nature of FRP materials, allowing for a smoother and more uniform load transfer [24]. In addition, adhesively bonded connections provide higher joint efficiencies and stiffness, which can be particularly important for the serviceability design of GFRP structures, generally governed by deformability requirements. Bonded joints are also lighter and potentially more durable because they do not require drilled holes that are weak points for moisture ingress. In spite of such advantages, the use of adhesive bonding in civil engineering applications is much rarer than bolting due to the following reasons: (1) difficulty in guaranteeing the necessary quality control conditions, particularly on construction sites,

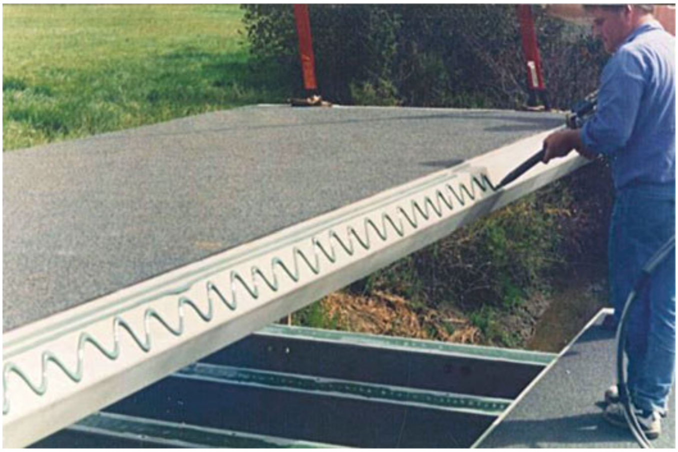

Fig. 11.32 Bonded connections between GFRP panels of bridge decks (courtesy of Creative Pultrusions)

(2) relatively high thickness of the FRP adherends, (3) lack of design guidance, (4) lack of comprehensive data about long-term durability and (5) concerns about high temperature behaviour. Adhesively bonded connections have been used mainly in bridge decks in order to join adjacent GFRP panels (Fig. 11.32) and also to join them to the longitudinal girders (Fig. 11.29). Adhesive bonding was also used in the *Eyecatcher* Building and in Lleida footbridge to assemble standard sections and obtain larger (stiffer and stronger) sections than those currently provided by composites manufacturers.

The use of bolted-bonded mixed connections generally does not increase the resistance of a corresponding simply bonded connection. Since the stiffness provided by conventional structural adhesives is considerably higher than that provided by the bolts, the adhesive sustains the vast majority of the applied load (in general, there is almost no load distribution between the adhesive and the bolts). Furthermore, bolts are usually positioned in the central part of the bonded overlap, where shear stresses are lower. The use of mixed connections may be justifiable in one of the following situations: (1) when bolts are expected to prevent the effects of a deficient bonding execution or adhesive deterioration during service life, (2) when the clamping pressure applied in the bolts is expected to improve the bonding performance and (3) when the adhesive is expected to help fulfilling deformability requirements (strength requirements may be fulfilled by bolts).

Interlocking connections comprise grooving and friction mechanisms that, in some cases, can be complemented with bolting and/or bonding. The main advantage of these modular construction systems is that they allow for very quick erection times, since the connections between FRP components are very easy to execute. However, high dimensional precision is required for the FRP components. An example of this connection method is the ACCS system (Advanced Composite Construction System), developed by Maunsells Structural Plastic Ltd. and used in

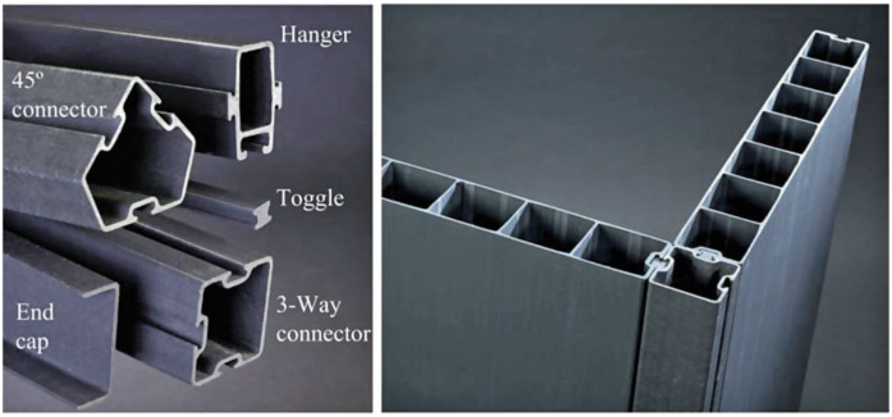

Fig. 11.33 Interlocking connections in the Advanced Composite Construction System (ACCS) (courtesy of Strongwell)

several pedestrian bridge decks, in which plank units (multicellular box sections) are assembled by sliding a toggle section into the groove of each panel (Fig. 11.33).

A priori, welding seems to be the most adequate method to join FRP materials, providing both economical and technical advantages. However, this technique is limited to FRP materials made of thermoplastic resins. As discussed above, these resins present several technical disadvantages when compared with thermoset resins (in terms of processing, fibre adhesion and impregnation, and mechanical properties), and this explains why they are very seldom used in civil engineering structural applications.

11.4.6 Regulation for GFRP Pultruded Profiles

Presently, most structural designs are made based on manufacturers' design guides, usually presented in the format of design tables, which are sometimes incomplete and/or over conservative. The Eurocomp Design Code and Handbook [16], published in 1996, provides design recommendations for polymeric composites; nevertheless, from a formal point of view, this document is not official (normative) nor does it address specifically GFRP pultruded profiles. In 2002, CEN published the European Standard EN 13706 [15], which defines a set of specifications for pultruded profiles. This standard establishes the test methods to determine several material properties (mechanical, physical and thermal), and it further defines two grades of profiles, specifying the minimum material properties a profile has to exhibit in order to be included in those grades. However, this document provides no design guidance. In 2007, the Italian National Research Council published the first normative recommendations for the design of structures made of FRP pultruded profiles [18]; however, these recommendations are only valid in Italy and to some extent they are still incomplete (as an example, in what concerns connections).

11.5 FRP Rebars

11.5.1 Geometries of FRP Rebars

FRP bars[12] produced by most composites manufacturers comprise fibres (generally, glass, carbon or aramid) oriented exclusively in the axial direction and embedded in a polymeric matrix (typically, vinylester or epoxy). For civil engineering applications, the most frequently used FRP bars are constituted by glass fibres and vinylester and are manufactured by pultrusion.[13]

The typical length of off-the-shelf FRP bars ranges between 10 and 14 m and their nominal diameters vary between 6 and 36 mm. The mechanical adherence or bond between FRP bars and the material to be reinforced strongly depends on the surface roughness of the bars. Therefore, the type of finishing or deformation system of the FRP rebar is a very important parameter in several applications. The surface of FRP bars can be produced with the following types of finishing (texture): (1) smooth, (2) surface formed deformations or ribs, (3) sand coatings and (4) exterior wound fibres, usually with additional sand coatings.

Conventional FRP bars are produced by standard pultrusion with straight geometry and are used to resist axial stresses. Additionally, it is possible to manufacture straight bars with anchorage heads and bent bars (U shaped) for shear reinforcement of concrete members (Fig. 11.34). In this case, the bars are bent (in the pultrusion plant) while the resin matrix is still uncured. After the resin cures, it is no longer possible to bend/unbend the bars, either mechanically or thermally (this would also cause the thermal decomposition of the resin). Therefore, the anchorage of the extremities of longitudinal bars is often made with prefabricated hooks, which are overlapped to the longitudinal bars in a certain length. It is worth mentioning that FRP bars can be easily cut with a diamond blade saw.

11.5.2 Typical Properties of FRP Rebars

Physical and mechanical properties of FRP rebars depend on several factors, namely, the volume, the orientation and the type of fibres, the type of resin, the geometry of the rebar and the quality control in the fabrication. Table 11.5 presents

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[12] In addition to FRP rebars, there are other types of reinforcing products, namely grids, bars with different cross-sections, cables (used in prestress) and meshes. These types of reinforcing products are much less often used in civil engineering structural applications and hence will not be addressed in this chapter.

[13] FRP rebars can also be produced by braiding and weaving.

Fig. 11.34 Different geometries of FRP bars: (**a**) straight bar, (**b**) bar with anchorage head, (**c**) bent bar (courtesy of Schöck)

Table 11.5 Typical physical and mechanical properties of FRP rebars (adapted from [7, 2])

Property		Test standard	GFRP	CFRP	AFRP
Density [g/cm^3]		ISO 1183, ASTM D 792	1.25–2.10	1.50–1.60	1.25–1.40
Fibre content [%]		ISO 1172, ASTM D 3171	50–60	50–60	–
Thermal expansion coefficient [$\times 10^{-6}$/°C]	Axial	ISO 11359-2, ASTM D 696	6.0–10.0	−9.0 to 0.0	−6.0 to −2.0
	Transverse		21.0–23.0	74.0–104.0	60.0–80.0
Axial tensile strength [MPa]		ISO 527, ASTM D 7205	483–1,600	600–3,690	1,720–2,540
Axial elasticity modulus [GPa]			35–51	120–580	41–125
Maximum axial strain [%]			1.2–3.1	0.5–1.7	1.9–4.4

typical ranges of variation for several physical and mechanical properties of FRP bars[14] made of glass (GFRP), carbon (CFRP) and aramid (AFRP) reinforcement.

The density of all types of FRP reinforcing bars is much lower (1/6–1/4) than that of steel bars (again, the main competitor) and their lightness facilitates transport and handling operations on the construction site. The thermal expansion coefficients of FRP bars[15] depend basically on the fibres and the resin, and this explains the different values in the axial and transverse directions. Unlike GFRP bars, CFRP and AFRP bars have negative thermal expansion coefficients in the axial direction. Finally, one should note that for high temperature variations, the high thermal expansion coefficient in the transverse direction may cause the longitudinal separation between the FRP bar and concrete, especially if the concrete cover is low [2].

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[14] According to the American Concrete Institute [2], in what concerns mechanical strength, manufacturers often indicate "guaranteed" values, whose exceedance probability is higher than 99.87 %.

[15] As a reference, the thermal expansion coefficient of concrete varies between 7.2×10^{-6} and 10.8×10^{-6}/°C.

In terms of mechanical behaviour in tension, regardless of the fibre reinforcement type, FRP bars present linear elastic behaviour up to failure (without any ductility), exhibiting very high tensile strength (well above that of conventional steel bars). In opposition to steel, the strength of FRP bars may vary with the diameter, particularly in GFRP bars. The elasticity modulus of FRP bars is very much dependent on the type of fibre. In GFRP bars (the ones most frequently used in civil engineering applications), it is only about 20–30 % that of steel. When using GFRP bars to reinforce concrete members, such a low elasticity modulus has consequences in terms of serviceability design, namely in terms of deformability and crack pattern.

The few studies performed so far about the compressive properties of FRP bars have indicated that their elasticity modulus and strength in compression can be considerably lower than in tension, especially in GFRP and AFRP bars. This explains why the use of FRP bars in columns or as compression reinforcement of flexural members is not recommended [2].

Because there is usually no reinforcement between layers of axial fibres, FRP bars generally present relatively low interlaminar shear strength. Therefore, under shear loads the performance of FRP bars depends essentially on the resin matrix. The shear resistance of FRP bars can be improved with the introduction of continuous strand mats in the fibre architecture, and the braiding or winding of fibres in the transverse direction [2].

The bond performance is a critical issue when FRP bars are used to reinforce concrete structures. Such performance depends on several aspects, including the mechanical properties of the bar and its surface roughness. Presently, the bond performance of several FRP bars is already comparable to that of steel bars [56].

Regarding long-term performance, as for other FRP materials, FRP bars resist corrosion and are electromagnetically transparent. However, several studies have shown that the mechanical properties of FRP bars can be considerably affected when they are subjected to moisture, alkaline, acid or saline solutions [52]. Unlike steel bars, FRP bars are susceptible to creep rupture under constant loads. Such susceptibility depends on the load level, environmental conditions and type of fibre reinforcement, with glass and carbon fibres being, respectively, the most and least susceptible [2]. Similarly to other FRP materials, the mechanical and bond performance of FRP bars is severely reduced at high temperatures and this needs to be considered when FRP reinforced members have to be designed for fire [51].

11.5.3 Advantages and Difficulties in the Use of FRP Rebars

The main advantages of FRP bars compared with conventional steel rebars used in concrete reinforcement are the following [2]: (1) high tensile strength in the longitudinal direction, (2) corrosion resistance, (3) lightness, (4) electromagnetic transparency, (5) high fatigue strength (yet dependent on the type of fibre reinforcement) and (6) low thermal and electric conductibility (for glass and aramid fibre reinforcement).

On the other hand, the following disadvantages arise when using this type of reinforcing rebars [2]: (1) linear elastic behaviour up to failure, which occurs in a brittle way (no ductility); (2) low elasticity modulus (varying with the type of fibre reinforcement); (3) low strength in the transverse direction; (4) susceptibility of polymeric resins and fibres to UV degradation (only relevant when FRP rebars are used as external strengthening elements); (5) limited durability of glass fibres in moist environments; (6) limited durability of some types of glass and aramid fibres to alkaline environments; (7) high thermal expansion coefficient in the transverse direction (with respect to the fibres direction), when compared to concrete; and (8) the mechanical performance reduction for high temperatures (dependent on the type of matrix), which may determine increasing the concrete cover.

11.5.4 Field of Application of FRP Rebars

The main features that justify selecting FRP bars (instead of steel) are their non-corrodibility and lack of electromagnetic interference, as well as their high tensile strength. Accordingly, FRP bars have been mostly used to reinforce concrete structures located in maritime environments (e.g. piers), bridge decks or other components subjected to de-icing salts (Fig. 11.35a, b), waste water treatment plants and structures enclosing equipment sensitive to electromagnetic fields, such as MRI facilities. FRP bars also have some potential for underground or buried structures, where they have been used in tunnelling works (e.g. shaft walls) and retention walls (Fig. 11.35c). Compared to steel bars, the main advantages of FRP bars in these applications are the improved corrosion resistance, the lightness that facilitates the lifting and handling of reinforcement cages, and since they are easier to cut the drilling operations in tunnels are facilitated.

Most of the applications described above involve GFRP bars, since they are more economical compared to other types of FRP bars. CFRP bars are generally used for concrete strengthening according to the NSM technique or for external prestressing. Besides being used to reinforce or strengthen concrete members, FRP bars have also been used in the rehabilitation of masonry and timber structural

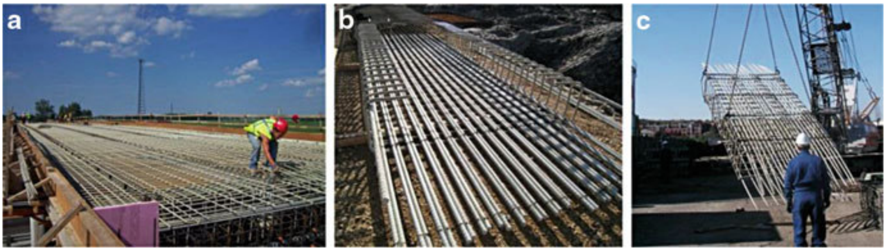

Fig. 11.35 Application of FRP bars in the reinforcement of (**a**) bridge deck, Canada; (**b**) fish farm inlet to sea, Portugal; (**c**) tunnel soft eye, Belgium (courtesy of Hughes Brothers)

elements. One possible application involves using GFRP bars and epoxy resin to connect (prosthesis) timber parts.

11.5.5 Application Process of FRP Rebars

The application process of FRP bars for the reinforcement of concrete members, including the handling and placement operations, is very similar to that of steel bar reinforcement. Guidance on the delivery, storage, handling, permitted damage tolerances, bar supports, placement tolerances and concrete cover is provided in several documents (e.g. ACI 440.1R-06 [2], FIB Bulletin 40 [30], CAN/CSA S806-02 [26]). If FRP bars have to be cut, diamond blades, grinders or fine blade saws can be used. The anchorages at the extremities of the rebars are generally made with prefabricated hooks overlapping the longitudinal rebars (bending operations on site are not possible). To keep the bars together, non-metal fixings or ties (e.g. plastic coated tie wire, nylon zip ties, plastic bar clips) are recommended.

11.5.6 Regulation for FRP Rebars

There are already several standards and guidelines for the design and construction of concrete structures reinforced with FRP rebars. In particular, the following documents are worth being mentioned:

- "Fib Bulletin 40—FRP reinforcement in RC structures", International Federation for Structural Concrete (2007) [30]
- "Guide for the Design and Construction of Concrete Structures Reinforced with Fibre-Reinforced Polymer Bars", Italian National Research Council (2007) [17]
- "ACI 440.1R-06—Guide for the Design and Construction of Structural Concrete Reinforced with FRP Bars"—American Concrete Institute 440 (2006) [2]
- "CAN/CSA-S6-02—Design and Construction of Building Components with Fibre-Reinforced Polymers"—Canadian Standards Association (2002) [26]
- "Recommendation for Design and Construction of Concrete Structures using Continuous Fiber Reinforcing Materials", Japan Society of Civil Engineers (1997) [39]

As for concrete structural elements reinforced with steel rebars, the design recommendations provided in the aforementioned documents are based in equilibrium and compatibility principles, together with the constitutive relations of the materials. However, as already mentioned, the mechanical behaviour of FRP rebars is substantially different from that of steel rebars; hence, the design philosophy for designing concrete structures reinforced with FRP bars is also different. FRP materials exhibit no plasticity, presenting linear elastic behaviour up to failure; therefore, the procedure used for flexural design needs to take into account such lack of ductility. On the other hand, the anisotropy of FRP materials affects their shear strength, the dowel effect and even their adherence to concrete.

In spite of the above-mentioned differences, the general methodology used for flexural design is similar to that used in the design of concrete members reinforced with steel rebars and, for the most part, calculations are based on the same assumptions. For ultimate limit states,[16] flexural members are designed for two possible failure modes: (1) tensile failure of the FRP reinforcement and (2) concrete crushing, in which members may still exhibit some (limited) plasticity. The first mode, albeit fragile, occurs after extensive cracking takes place and for a significant deformation of the members, stemming from the high deformation capacity of FRP rebars. For service limit states,[17] cracked stiffness is generally low and therefore design may be governed by deformability restrictions. However, in general, if cross sections are designed to fail due to concrete crushing, serviceability requirements (deformation, cracking) are generally fulfilled [2]. Shear design is also very similar to that of concrete members reinforced with steel stirrups. However, one should take into account the different mechanical properties of FRP rebars [2].

11.6 FRP Strengthening Systems

11.6.1 Geometries of FRP Strengthening Systems

FRP systems used in structural strengthening are available in a wide range of shapes. However, the following two main typologies can be identified: (1) wet layup systems, cured in situ (Fig. 11.36a), and (2) precured systems (Fig. 11.36b, c).

Wet layup systems comprise mats of uni- or multidirectional (sheets or fabrics) dry and flexible fibres, with widths that can vary between 0.15 and 1.50 m. These systems are applied by moulding these reinforcing mats around the external surface of the element to be strengthened. In this type of application, the FRP system cures and hardens at the job site, at ambient temperature, through the saturation of the mats with epoxy or vinylester resins, which also guarantee the proper bonding between the FRP element and the member to be strengthened. As an alternative, the mats can be pre-impregnated with resin and partially cured in a plant. In this case, they can be applied to the surface of the structural member to be strengthened without any additional resin. However, this operation requires heat supply in order to complete the curing process.

Precured systems generally comprise precured (hardened) FRP strips that are directly bonded with epoxy adhesive to the external surface of the member to be

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[16] Ultimate limit states design implies the maintenance of the equilibrium and strength capacity of the structure.

[17] Service limit states design includes the fulfilment of limits for deformations, vibrations and crack widths and is associated with durability, appearance, visual comfort and functionality requirements of structures.

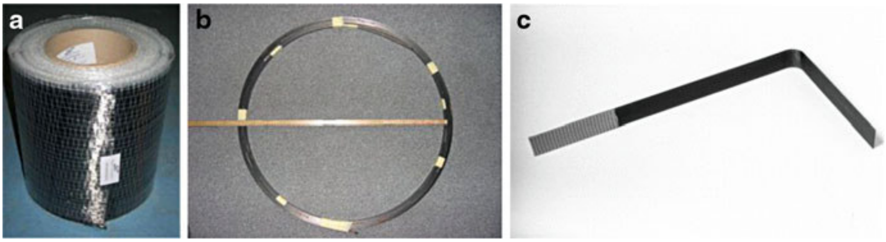

Fig. 11.36 Different typologies of CFRP strengthening elements: (**a**) sheets, (**b**) straight (roll) strips and (**c**) L-shaped strips (courtesy of Sika)

strengthened, according to the externally bonded reinforcement (EBR) technique. These strips are typically produced by pultrusion, with widths and thickness that usually range between 50 and 100 mm and 1.0 and 2.0 mm, respectively. In addition to current strips with flat cross section, some manufacturers also produce L-shaped strips for shear strengthening and shell segments for column/pile strengthening.

More recently, a variant technique to EBR was developed, called near-surface mounted (NSM) technique. This technique consists of inserting thin and narrow strips (width between 3 and 18 mm) or circular or rectangular bars into grooves opened on the concrete cover of the structural member to be strengthened.

In most products commercially available, the FRP strips of sheets are made of carbon or glass fibres, embedded in epoxy or vinylester resin matrix. In the case of strips, fibres are oriented in the longitudinal direction, whereas for mats, fibres may be also oriented in other directions.

11.6.2 Typical Properties of FRP Strengthening Systems

Tables 11.6 and 11.7 present typical ranges of variation for physical and mechanical properties of FRP[18] strips and mats, respectively, used in the strengthening of existing structures. In general (except when stated otherwise), the values presented in those tables correspond to FRP composites made of epoxy resins and conventional fibres (in the case of strips) and unidirectional fibres (in the case of mats).

11.6.3 Advantages and Difficulties in the Use of FRP Strengthening Systems

The use of FRP systems for structural strengthening developed mainly after the decade of 1980, based on the experience obtained from steel plate bonding. This

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[18] According to the ACI Committee 440 [3], in what concerns strength, and similarly to FRP rebars, manufacturers generally indicate "guaranteed" values, whose exceedance probability is higher than 99.87 %.

Table 11.6 Typical physical and mechanical properties of FRP strips (adapted from [7])

Property	Test standard	CFRP	CFRP[a]	CFRP[b]	GFRP
Fibre content [%]	ISO 1172, ASTM D 3171	65–70	65–70	60	65–70
Nominal thickness [mm]	–	1.2–1.9	1.2	2.0	1.4–1.9
Width [mm]	–	50–120	50–120	16	50–120
Axial tensile strength [MPa]	ISO 527, ASTM D 638, ASTM D7565	2,690–2,800	1,290	2,070	90
Axial elasticity modulus [GPa]		155–165	300	131	41
Maximum axial strain [%]		1.8	–	1.7	2.2

[a]High-modulus fibres
[b]Vinylester resin

Table 11.7 Typical physical and mechanical properties of FRP mats (adapted from [7])

Property	CFRP	CFRP[a]	CFRP	GFRP
Nominal thickness [mm]	0.165–0.330	0.165	–	0.356
Width [mm]	600	600	–	1,200
Fibre architecture	Unidirectional	Unidirectional	Multidirectional	Unidirectional
Axial tensile strength (of the fibres) [MPa]	3,790	3,520	3,500	1,520–3,240
Axial elasticity modulus (of the fibres) [GPa]	230	370	230	72
Maximum axial strain [%]	1.67–1.70	0.94	1.7	2.1–4.5

[a]High-modulus fibres

latter strengthening technique, used since the 1960s, and concrete jacketing are the main alternatives to FRP strengthening systems for civil engineering applications.

The main advantages of FRP strengthening systems over alternative traditional strengthening solutions (e.g. concrete jacketing and steel plate bonding, its main competitor) are the following: (1) very high tensile strength; (2) high elasticity modulus (when carbon fibres are used)[19]; (3) relatively high deformation capacity; (4) low self-weight, facilitating on site application, reducing the labour costs, as well as the increase of weight in the existing structure; (5) non-corrodibility; and (6) wide range of FRP geometries and dimensions commercially available.

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[19] Nevertheless, due to the very low thickness of FRP strengthening systems their contribution to overall stiffness increase is generally low, particularly for concrete members.

When using FRP strengthening systems, some difficulties also have to be faced, namely the following: (1) linear-elastic behaviour up to failure, which generally limits the ductility of the element to be strengthened; (2) limited exploitation of material performance caused by premature adherence failure mechanisms (that can be hampered with appropriate anchorage devices); and (3) remarkable reduction of strength, stiffness and bond properties of CFRP systems at moderately elevated temperatures, which can make it necessary to use appropriate thermal insulation when designing for the fire load combination [4, 33, 64]. The above-mentioned limitations, being intrinsic to the nature of FRP materials, are to some extent similar to those already described for FRP profiles and bars.

11.6.4 Field of Application of FRP Strengthening Systems

FRP strengthening systems are already a well-established “state-of-the-art” technique for rehabilitation applications. After more than 30 years since they were first used, there are now numerous applications of FRP strengthening systems in buildings and bridges, aiming at increasing their load capacity for both static (permanent and live) and dynamic loads (typically seismic retrofitting).

FRP strengthening systems have been used with different materials, including reinforced concrete, steel, iron, masonry and timber. The type of structural elements that have been strengthened with FRP systems include beams, slabs, columns, beam-column joints, walls, chimneys, arches, domes and tunnels.

In most cases, FRP systems are used to strengthen reinforced concrete members with the following goals: (1) flexural strengthening of beams and slabs (Fig. 11.37a–c); (2) shear strengthening of beams (Fig. 11.37d); and (3) axial/flexural strengthening and confinement of columns (Fig. 11.38), aiming at increasing their transverse deformation capacity and ductility and axial strength.

11.6.5 Application Process of FRP Strengthening Systems

Prior to the installation of the FRP strengthening systems, there is a set of preliminary works that may be needed, namely the following: removal of degraded (minimum substrate tensile and compressive strengths of respectively 1.5 and 15 MPa are required) or contaminated (carbonation/chlorides) concrete; repair, cleaning, protection and/or addition of reinforcing rebars; reconstitution of concrete sections with mortars, micro-concrete or concrete (depending on the volume that needs to be restored); and sealing or injection of cracks wider than 0.5 mm.

Fig. 11.37 Flexural strengthening of (**a**) beams, (**b**) slabs with strips, (**c**) slabs with sheets and (**d**) flexural and shear strengthening of a beam with sheets (adapted from [55, 10, 9, 58])

Fig. 11.38 Flexural and axial (confinement) strengthening of (**a**) columns and (**b**) chimneys with strips and sheets; use of sheets in (**c**) columns and (**d**) walls (adapted from [55, 10, 35])

For FRP strengthening systems applied according to the EBR technique, in order to guarantee good adherence to the substrate, the following surface preparation is necessary for both FRP strips (precured systems) and sheets (wet layup systems): (1) surface roughening causing a minor exposure of the aggregates, using either

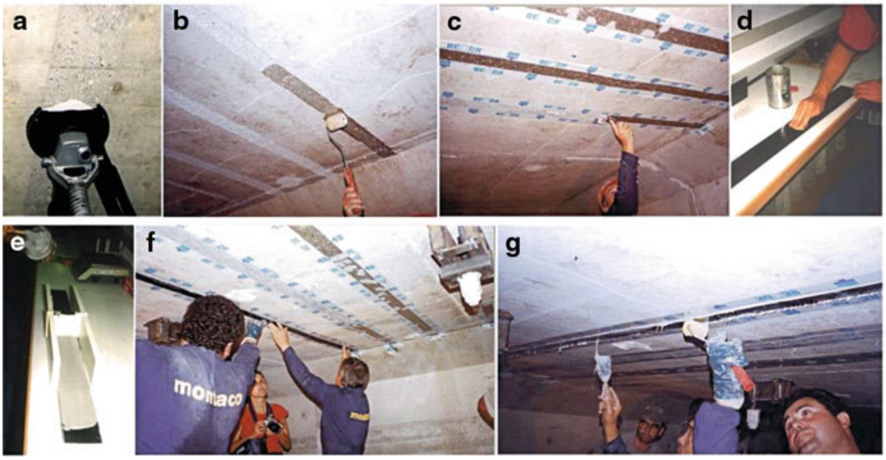

Fig. 11.39 Different stages of the application of a precured FRP system in the strengthening of a reinforced concrete slab, according to the EBR technique (adapted from [10, 29]). (**a**) Surface roughening; (**b**) application of primer; (**c**) application of regularization mortar; (**d**) cleaning the FRP laminate; (**e**) application of adhesive on the FRP laminate; (**f**) application of the FRP laminate; (**g**) application of pressure and removal of the squeezed adhesive

sandblasting, water jet, needle scalers or emeries (Fig. 11.39a)—a roughness degree of 0.3 mm is often required; (2) rounding of the substrate edges (minimum radius of 10 mm), whenever the strengthening system is to wrap the reinforced concrete member; (3) possible removal or correction of out-of-plane variations by respectively grinding or applying a regularization mortar ("putty") in voids and smooth surface discontinuities, namely, in concave surfaces (Fig. 11.39c); the maximum recommended unevenness in a 2.0 m base is 10 mm (strips) and 4 mm (sheets); (4) cleaning of the substrate using a jet of compressed air (paint, oil, release agents or other compounds that may affect the bond must also be removed with an appropriate method); and (5) optionally (if specified by the manufacturer), application of a primer, which fills the substrate pores and increases the FRP-concrete adherence (Fig. 11.39b).

After performing the above-mentioned surface preparation works, the installation of FRP strips involves the following steps: (1) cutting and cleaning (with acetone or diluent) the FRP strips (Fig. 11.39d); (2) mixing and application of the adhesive on the surface of the strip (a domed shape is recommended to prevent voids) (Fig. 11.39e) and on the concrete substrate; (3) manual application and adjustment of the strip to the substrate (Fig. 11.39f); and (4) application of pressure with a rigid rubber roller (final adhesive thickness ranging between 1 and 3 mm) and removal of the adhesive that is squeezed laterally with a spatula (Fig. 11.39g).

In what concerns the FRP sheets, after the surface preparation procedures described above, each sheet is installed as follows: (1) application of a first layer of adhesive, directly over the substrate and/or over the FRP sheet; (2) application of

Fig. 11.40 Different stages of the application of a precured FRP system in the strengthening of a reinforced concrete element, according to the NSM technique [11]. (**a**) Execution of grooves cut onto the concrete cover; (**b**) cleaning of the groove; (**c**) mixing the adhesive; (**d**) filling the groove with the adhesive; (**e**) introduction of the FRP laminate into the groove

the FRP sheet on the substrate (transverse overlap between sheets of 0.10 m), first adjusting the sheet manually and/or with a rubber trowel and then applying pressure with a ribbed rigid roller, so that the FRP sheet is stretched; (3) application of a second layer of (impregnation) adhesive and further pressing of the FRP sheet; and (4) repetition of the above-mentioned steps for further layers.

After applying either the FRP strips or sheets, optionally, a cover layer (e.g. painting, mortar, concrete, panels) can be applied with aesthetic or environmental protection function (e.g. UV or fire protection).

For any of the above-mentioned techniques, the correct application is crucial for the good structural performance of the strengthening system [41]. Therefore, in terms of quality control, there is a set of procedures and verifications that need to be made, namely the following: (1) assessment of the quality of the concrete that is to be strengthened, in what concerns its superficial tensile strength, cracking pattern and spalling due to rebar corrosion, smoothness, cleanness and moisture level; (2) environmental conditions, in particular, the minimum and maximum temperatures and relative humidity; and (3) quality of the bonding, which may be assessed by means of acoustic tests or pull-off tests.

In NSM strengthening systems, the installation of the FRP elements (strips or rods) is performed as follows: (1) execution of grooves cut onto the concrete cover with a circular saw blade (Fig. 11.40a), (2) cleaning of the groove with compressed air (Fig. 11.40b), (3) cutting and cleaning the FRP strengthening element, (4) mixing the adhesive (Fig. 11.40c) and filling the groove with the adhesive (Fig. 11.40d), (5) application of adhesive in the FRP strengthening element (for strips, in both faces) and (6) introduction of the FRP strengthening element inside the groove and removal of the adhesive in excess (Fig. 11.40e).

In addition to the more current techniques described above, some special techniques have been recently developed, some of which are patented by FRP strengthening system suppliers. The two following special techniques are mentioned [29]: (1) automated wrapping of dry or *prepreg* tows and sheets, most often used in column strengthening (winding), and the (2) application of prestressed FRP systems [34], which has been applied in the strengthening of both beams and slabs.

11.6.6 Regulation for FRP Strengthening Systems

Although FRP systems may be used to strengthen different structural materials, presently, standards and design guidelines are only available for reinforced concrete elements. The following documents provide detailed information concerning the design, application, constructive details and quality control of FRP strengthening systems:

- "ACI 440.2R-08—Guide for the Design and Construction of Externally Bonded FRP Systems for Strengthening Concrete Structures"—American Concrete Institute (2008) [3]
- "TR 55—Design Guidance for Strengthening Concrete Structures Using Fibre Composite Materials"—The Concrete Society (2004) [61]
- "Fib Bulletin 14—Externally Bonded FRP Reinforcement for RC Structures", International Federation for Structural Concrete (2001) [29]
- "Recommendation for Upgrading of Concrete Structures with Use of Continuous Fiber Sheets", Japan Society of Civil Engineers (2001) [40]

In terms of structural principles, FRP strengthening is very similar to steel plate bonding, differing in the following aspects: the strengthening material/system (1) is linear elastic up to failure, (2) has much higher tensile strength and (3) presents higher susceptibility to premature failure modes by debonding, which are generally associated to relatively low strains in the FRP material, motivating the need and interest in using adequate anchorage systems.

When FRP systems are used for flexural strengthening [29, 3], the cross-sectional analysis and member design procedures are also based on equilibrium and compatibility principles, together with the constitutive relations of the materials, assuming that (1) no slip develops at the FRP-concrete interface and (2) the adhesive does not deform due to shear. It is important to take into account the initial (already installed) stresses and deformations of the elements prior to the application of the strengthening system. The failure modes in bending include the tensile failure of the FRP system, its debonding from the substrate (which may occur in different ways) and concrete crushing. Any of these failure modes can occur before or after the yielding of steel rebars. In general, the preferred failure mode corresponds to concrete crushing with yielding of the steel rebars and maintenance of the adherence of the FRP system. In most design guidelines and recommendations [29, 3], the strength increase is limited in order to guarantee a residual strength capacity in case of premature debonding or failure of the strengthening system due to accidental loads (e.g. fire) or vandalism. On the other hand, to prevent premature debonding of the strengthening system, the maximum strain in the FRP element is usually limited to values well below the ultimate tensile strain.

In terms of shear strengthening, the capacity of a strengthened member is determined from the sum of the individual contributions provided by the FRP system, the concrete and the steel stirrups. Such FRP contribution is generally computed using (Mörsh's) truss model, according to the same general principles used to determine the shear strength provided by the steel stirrups.

Finally, in what concerns column strengthening, the above-mentioned documents present design equations, based on analytical formulations and results of experimental tests, that allow determining the increase in strength and ductility (due to the confinement provided by FRP systems) of elements subjected to compression or bending and compression.

Sources of Further Information

Key Books

- Starr TF (2000) Pultrusion for engineers. Woodhead Publishing Limited, Cambridge.
- Peters ST (1998) Handbook of composites. Chapman & Hall, London.
- Strong AB (2008) Fundamentals of composites manufacturing: materials, methods and applications. Society of Manufacturing Engineers, Dearborn, MI.
- Bank LC (2006) Composites for construction. Structural design with FRP materials. Wiley, Hoboken, NJ.
- Teng JG (2002) FRP-strengthened RC structures. Wiley, Chichester.

Series of Proceedings

- International conference on Fiber Reinforced Polymer (FRP) Composites in Civil Engineering (CICE).
- International Symposium on Fiber Reinforced Polymer Reinforcement for Concrete Structures (FRPRCS).
- Advanced Composite Materials in Bridges and Structures (ACMBS).
- Durability of Fibre Reinforced Polymer (FRP) Composites for Construction (CDCC).
- International Conference on Composite Materials (ICCM).
- European Conference on Composite Materials (ECCM).
- Advanced Composites in Construction Conference (ACIC).
- International Conference on Composite Structures (ICCS).

Major Trade/Professional Bodies

- American Composites Manufacturers Association (ACMA).
- European Pultrusion Technology Association (EPTA).
- ALTO, Perfis Pultrudidos Lda.
- Bedford Reinforced Plastics Inc.
- Creative Pultrusions Inc.

- Exel Composites UK.
- Fiberline Composites.
- Fyfe Co. LLC.
- Hughes Brothers.
- Martin Marietta Composites.
- Pultrall.
- Sika.
- Schöck.
- Strongwell Corporation.
- S&P Clever Reinforcement.
- Top Glass, S.P.A.

Research and Interest Groups

- American Concrete Institute (ACI)—Committee 440 (Fiber-Reinforced Polymer Reinforcement).
- Fédération International du Béton (FIB)—Task Group 9.3 (FRP Reinforcement for Concrete Structures).
- International Association for Bridge and Structural Engineering, IABSE—Working Commission 8 (Fibre Reinforced Composite Structures).
- International Institute for FRP in Construction (IIFC).
- ISIS Canada Research Network.

Websites/Online Videos

- http://www.pultrusions.org/
- http://www.pultruders.com/
- http://www.compositesworld.com/
- http://www.reinforcedplastics.com
- http://www.videosurf.com/videos/pultrusion

References

1. ACI Committee 440 (1996) State-of-the-art report on fiber reinforced plastic (FRP) reinforcement for concrete structures, ACI 440 R-96. American Concrete Institute, Farmington Hills, MI
2. ACI Committee 440 (2006) Guide for the design and construction of structural concrete reinforced with FRP bars, ACI 440.1R-06. American Concrete Institute, Farmington Hills, MI
3. ACI Committee 440 (2008) Guide for the design and construction of externally bonded FRP systems for strengthening concrete structures, ACI 440.2R-08. American Concrete Institute, Farmington Hills, MI, p 76
4. Ahmed A, Kodur VKR (2011) Effect of bond degradation on fire resistance of FRP-strengthened reinforced concrete beams. Compos Part B Eng 42(2):226–237

5. ASCE (2013) Report card for America's infrastructure, 2013. American Society of Civil Engineers. http://www.infrastructurereportcard.org/bridges/
6. Bakis CE, Bank LC, Brown VL, Cosenza E, Davalos JF, Lesko JJ, Rizkalla SH, Triantafillou TC (2000) Fiber-reinforced polymer composites for construction—state-of-the-art review. J Compos Constr 6:73–87
7. Bank LC (2006) Composites for construction: structural design with FRP materials. Wiley, Hoboken, NJ
8. Barbero EJ (1998) Introduction to composite materials design. Taylor & Francis, Philadelphia, PA
9. Bettor MBT (2003) MBrace Composite system for structures strengthening (in Spanish)
10. Bettor MBT Portugal (1999). MBrace composite system. Technical sheets (in Portuguese)
11. Bonaldo E (2008) Composite materials and discrete steel fibres for the strengthening of thin concrete structures. PhD thesis in Civil Engineering, Minho University
12. Braestrup M (1999) Footbridge constructed from glass-fiber reinforced profiles, Denmark. Struct Eng Int 9:256–258
13. Burgoyne C (1999) Advanced composites in civil engineering in Europe. Struct Eng Int 9:267–273
14. Busel JP, Lockwood JD (2000) Product select guide: FRP composite products for bridge application. The Market Development Alliance of the FRP Composites Industry, Harrison, NY
15. CEN (2002) EN 13706: Reinforced plastics composites — Specifications for pultruded profiles. Part 1: Designation; Part 2: Methods of test and general requirements; Part 3: Specific requirements. European Committee for Standardisation, Brussels
16. Clarke JL (ed) (1996) Structural design of polymer composites—EuroComp design code and handbook. E & FN Spon, London
17. CNR (2007) National Research Council of Italy, guide for the design and construction of concrete structures reinforced with fiber-reinforced polymer bars. Advisory Committee on Technical Recommendations for Construction, Roma
18. CNR (2008) National Research Council of Italy, guide for the design and construction of structures made of FRP pultruded elements. Advisory Committee on Technical Recommendations for Construction, Roma
19. Conroy A, Halliwell S, Reynolds T (2006) Composites recycling in the construction industry. Compos Part A 37:1216–1222
20. Correia JR, Branco FA, Ferreira JG (2010) The effect of different passive fire protection systems on the fire reaction properties of GFRP pultruded profiles for civil construction. Compos Part A Appl Sci Manuf 41:441–452
21. Correia JR, Branco FA, Ferreira JG, Bai Y, Keller T (2010) Fire protection systems for floors of buildings made of GFRP pultruded profiles. Part 1: experimental investigations. Compos Part B Eng 43:1545–1556
22. Correia JR, Cabral-Fonseca S, Branco FA, Ferreira J, Eusébio MI, Rodrigues MP (2006) Durability of glass fibre reinforced polyester (GFRP) pultruded profiles for construction applications. Mech Compos Mater 42:325–338
23. Correia JR, Gomes M, Pires J, Branco FA (2013) Mechanical behaviour of pultruded glass fibre reinforced polymer composites at elevated temperature: experiments and model assessment. Compos Struct 98:303–313
24. Correia JR (2008) GFRP pultruded profiles in civil engineering: hybrid solutions, bonded connections and fire behaviour. PhD thesis in Civil Engineering, IST, Technical University of Lisbon
25. Creative Pultrusions Inc. (1999) The new and improved Pultex pultrusion design manual for standard and custom fiber reinforced polymer structural profiles. Alum Bank, PA., USA
26. CSA (2002) Canadian Standards Association, design and construction of building components with fibre-reinforced polymers, CAN/CSA S806-02. Canadian Standards Association, Rexdale, p 177
27. DPS Composites. www.dpscomposites.com. Accessed 6 July 2003

28. Ferreira JG, Branco FA (2007) Structural application of GRC in telecommunication towers. Constr Build Mater 21:19–28
29. FIB (2001) Externally bonded FRP reinforcement for RC structures, Bulletin 14. International Federation for Structural Concrete, Lausanne
30. FIB (2007) FRP reinforcement in RC structures, Bulletin 40. International Federation for Structural Concrete, Lausanne
31. Fiberline Composites (1995) Fiberline design manual. Middelfart, Denmark
32. Fiberline Composites (2003) www.fiberline.com. Accessed 5 June 2003
33. Firmo JP, Correia JR, França P (2012) Fire behaviour of reinforced concrete beams strengthened with CFRP laminates: protection systems with insulation of the anchorage zones. Compos Part B Eng 43(3):1545–1556
34. França P (2008) Reinforced concrete beams strengthened with prestressed CFRP laminates. PhD thesis in Civil Engineering, Technical University of Lisbon
35. Fyfe (2010) www.fyfeco.com. Accessed 25 Jan 2010.
36. Harries KA, Porter ML, Busel JP (2003) FRP materials and concrete—research needs. Concrete Int 25:69–74
37. Hayes MD (1998) Characterization and modeling of a fiber-reinforced polymeric composite structural beam and bridge structure for use in the Tom's Creek Bridge rehabilitation project. Master's thesis, Faculty of the Virginia Polytechnic Institute and State University, Blacksburg, VA
38. Hollaway LC (2003) The evolution of and the way forward for advanced polymer composites in the civil infrastructure. Constr Build Mater 17:365–378
39. JSCE (1997) Japan Society of Civil Engineers. Recommendation for design and construction of concrete structures using continuous fiber reinforcing materials. Concrete Engineering Series No. 23, Tokyo, p 325
40. JSCE (2001) Japan Society of Civil Engineers, recommendation for upgrading of concrete structures with use of continuous fiber sheets. Concrete Engineering Series No. 41, Tokyo
41. Juvandes L (1999) Strengthening and retrofitting of concrete structures using CFRP composite materials. PhD thesis in Civil Engineering, Porto University (in Portuguese)
42. Keller T, Bai Y, Vallée T (2007) Long-term performance of a glass-fiber-reinforced polymer truss bridge. J Compos Constr 11:99–108
43. Keller T (1999) Advanced materials: an introduction. Struct Eng Int 9:250
44. Keller T (1999) Towards structural forms for composite fibre materials. Struct Eng Int 9:297–300
45. Keller T (2002a) Fibre reinforced polymer materials in bridge construction. In: IABSE symposium, towards a better built environment—innovation, sustainability, information technology, Melbourne
46. Keller T (2002b) Overview of fibre-reinforced polymers in bridge construction. Struct Eng Int 12:66–70
47. Keller T (2003) Use of Fibre Reinforced Polymers in Bridge Construction. Structural engineering documents, vol 7. IABSE, Zurich
48. Kharbari VM, Chin JW, Hunston D, Benmokrane B, Juska T, Morgan R, Lesko JJ, Sorathia U, Reynaud D (2003) Durability gap analysis for fiber-reinforced polymer composites in civil infrastructure. J Compos Constr 7:238–247
49. Kharbari VM, Chin JW, Hunston D, Benmokrane B, Juska T, Morgan R, Lesko JJ, Sorathia U, Reynaud D (2001) Gap analysis for durability of fiber-reinforced polymer composites in civil infrastructure. The Civil Engineering Research Foundation, American Society of Civil Engineers. Washington, DC., USA
50. Liao K, Schultheisz CR, Hunston DL, Brinson LC (1998) Long-term durability of fiber-reinforced polymer matrix composite materials for infrastructure applications: a review. J Adv Mater 30:3–40

51. Nigro E, Cefarelli G, Bilotta A, Manfredi G, Cosenza E (2011) Fire resistance of concrete slabs reinforced with FRP bars. Part I: experimental investigations on the mechanical behaviour. Compos Part B Eng 42(6):1739–1750
52. Nkurunziza G, Debaiky A, Cousin P, Benmokrane B (2005) Durability of GFRP bars: a critical review of the literature. Prog Struct Eng Mater 7:194–209
53. Oates D (1990) Innovations in mud-brick: decorative and structural technique in ancient Mesopotamia. World Archaeol 21:388–406
54. Pickering SJ (2006) Recycling technologies for thermoset composite materials—current status. Compos Part A 37:1206–1215
55. S&P Clever Reinforcement (2010) www.sp-reinforcement.ch. Accessed 25 Jan 2010
56. Schöck Bauteile GmbH (2005) Technical information Schöck Combar—company brochure. Baden-Baden, Germany
57. Schuttle CL (1994) Environmental durability of glass-fiber composites. Mater Sci Eng 13:265–323
58. Sika (2010) www.sika.com. Accessed 25 Jan 2010
59. Sobrino JA, Pulido MDG (2002) Towards advanced composite material footbridges. Struct Eng Int 12:84–86
60. Tang B (1997) Fiber reinforced polymer composites application in USA. In: Proceedings of the First Korea/USA road workshop
61. TR55 (2004) Design guidance for strengthening concrete structures using fibre composite materials. The Concrete Society, Camberley
62. Tracy C (2005) Fire endurance of multicellular panels in an FRP building system. PhD thesis, École Polytechnique Fédérale de Lausanne
63. Vijay PV, GangaRao HVS, Bargo JM (2000) Mechanical characterization of recycled thermoplastic polymers for infrastructure applications. In: Proceedings of the third international conference on advanced composite materials in bridges and structures, Ottawa
64. Williams BK, Kodur VKR, Green MF, Bisby L (2008) Fire endurance of fiber-reinforced polymer strengthened concrete T-beams. ACI Struct J 105(1):60–67
65. Zhou A, Keller T (2005) Joining techniques for fiber reinforced polymer composite bridge deck systems. Compos Struct 69:336–345
66. Zureick A, Scott D (2000) Short-term behavior and design of fibre-reinforced polymeric slender members under axial compression. J Compos Constr 1:140–149

Wood

12

Helena Cruz, Dennis Jones, and Lina Nunes

Abstract

The growing diversity of wood products and their uses contradicts the idea that wood is a traditional material, which has always been used by humans with a minimum of modification, widely known and still mainly processed on an empirical knowledge basis. Since wood is a natural material, there is a plethora of information about its production, about the forestry concerns in environmental terms and the wood's value within the context of sustainability of the construction. Given the objectives of this publication, this chapter would cover mainly the aspects that can more directly help engineers and architects regarding the use of wood in construction. Together with a basic knowledge of the material, which is considered indispensable, a point has been made to provide guidelines for the selection of wood and its application in the construction industry.

Keywords

Wood • Timber • Wood products • Construction • Sustainability • Properties • Durability • Guidelines • Natural material • Variability • Wood defects • Wood moisture • Strength • Specification

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M.C. Gonçalves, F. Margarido (eds.), *Materials for Construction and Civil Engineering*, DOI 10.1007/978-3-319-08236-3_12

12.1 Introduction

The growing diversity of wood products and their uses contradicts ever more the idea that wood is a traditional material, which has always been used by humans with a minimum of modification, widely known, and still mainly processed on an empirical knowledge basis. It is interesting that this idea no longer corresponded to reality by the end of World War II, as new wood-based materials started to appear, along with the spread of new constructive systems and the development of more objective structural design rules, such that it is now completely outdated at the start of the twenty-first century.

Today we are witnessing a multiplicity of new engineered wood products, with very interesting features with regard to shape, dimensions, appearance and, especially, physical and mechanical characteristics. Joining techniques have also undergone very important developments, manifested in the development of high-performance glues of great durability and in the development of more efficient connectors and connections.

Regarding the durability of wood, which is perhaps one of the aspects of greater concern, the majority of the species with commercial interest have been characterised in this regard, and we have the knowledge and the means to know under which conditions a particular wood species should be applied and/or in what way we can protect it in order to lengthen its service life. In the past few years there has been a significant development concerning the wood protection philosophy and the current methods of preservation and treatment towards an approach that is less aggressive to the environment and less toxic for humans.

Developments have also been made regarding the design of structures, and we have now at our disposal design rules and an extensive set of standards, which allows us to consider wood alongside other construction materials, as well as to specify the material and to characterise and verify its performance objectively.

Since wood is a natural material, there is a plethora of information about its production, about the forestry concerns in environmental terms and the wood's value within the context of sustainability of the construction. In historical terms, too, the use of wood, particularly in structures, is as rich as it is diverse and would merit further discussion. Nevertheless, given the objectives of this publication, it was understood that this chapter would cover mainly the aspects that can more directly help engineers and architects regarding the use of wood in construction.

More than giving a historical perspective on the use of wood, together with a basic knowledge of the material, which is considered indispensable, a point has been made to provide guidelines for the selection of wood and its application in the construction industry, and whenever possible, this has been framed within the normative documents that are currently applicable.

12.2 What Is Wood

Wood is a natural composite material of biological origin made of a heterogeneous and anisotropic substance that is elaborated by a living organism—the tree.

Although it is possible to make use of the resultant wood from pruning, most of the wood material being used comes from the tree's trunk. Besides supporting the organism during the tree's lifetime, by supporting its own weight and the actions applied to it such as wind and snow, the trunk ensures that the matters necessary to the process of photosynthesis (raw sap) and the storage of produced substances and water are carried out, even during the times of decreased physiological activity or total repose.

The wood (or woody tissue) is, thus, composed of small cellular elements with a predominantly longitudinal direction, classified according to the functions that they perform. Their whole and arrangement (anatomical structure) are characteristic of each forest species, though they may also vary, to a certain extent, according to age and growing conditions (soil, climate, altitude, forestry exploitation, fires, etc.).

From the chemical point of view, the cellular walls consist essentially of cellulose and hemicelluloses (approximately 40–50 % and 20–40 % of its composition, respectively) that are embedded in an amorphous matrix of lignin (approximately 15–35 %). In addition to these, wood possesses a set of organic compounds known as extractives (approximately 1–5 %), whose removal does not affect the material's physical and mechanical properties significantly [1, 2].

The diametrical growth of the tree is due to the addition of new cells that are generated by the cambium, which generates woody tissue to the inside as well as bark to the outside, while progressively moving away from the pith (Fig. 12.1).

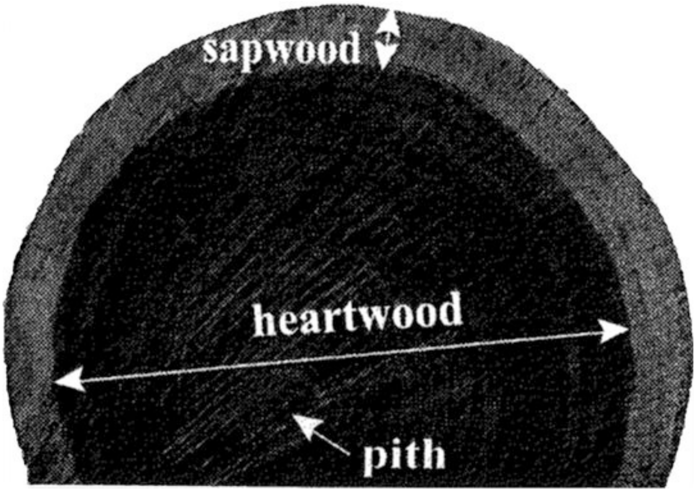

Fig. 12.1 Cross section of a hardwood trunk

Softwoods and Hardwoods

The cells of the woody tissue are differentiated into cellular elements with different physiological functions (sap conduction, structural support, storage, etc.), this variation being much greater in the case of hardwoods, resulting in more complex and diverse anatomical arrangements than those in the more ancestral softwoods.

The microscopic observation of the anatomical arrangements of wood such as of its type, dimensions and relative disposition of the cellular elements allows us to distinguish between woods that are obtained from different forest species. This method is thus generally used when one wants to verify or identify the species of origin of a given wood sample, a task that in many cases turns out to be impossible through the macroscopic analysis of the sample's texture.

Examples of softwood species include pine, fir and cedar and as for hardwood species, oak, chestnut tree, beech, eucalyptus as well as most of the species that are the sources of tropical timber we use.

While softwoods present a simple structure composed of tracheids (elongated cells that perform both the function of supporting the tree and transporting the raw sap to the crown) and parenchyma cells (where reserve nutritional substances are stored, such as starches and oils), the support functions of hardwoods' cells are designated by fibres. Those with transport functions are known as woody stems (Fig. 12.2). Within the terminology of wood as a construction material, the designation 'wood fibres' applies both to the tracheids of softwoods and the fibres of hardwoods.

Earlywood and Latewood

For the majority of trees in temperate zones, there is a slowdown or even a complete stop in the formation of wood during winter, followed by resumption at the onset of spring. At microscopic level this variation implies a difference in the diameter of

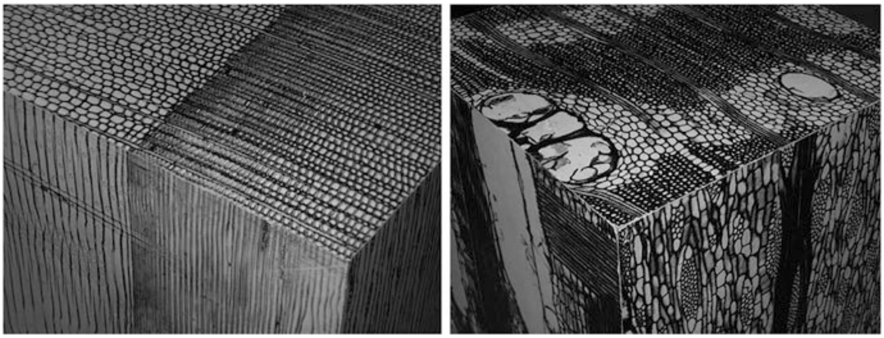

Fig. 12.2 Microscopic structure of softwood (*left*) and hardwood (*right*) [1]

the cells and in wall thickness, which, at macroscopic level, reflect differences in tone creating an alternation of pale and dark growth rings (early- and latewood rings). In such cases it is possible to estimate a tree's age by the number of annual growth rings, each of which corresponds to a set composed of an early- and latewood rings.

In some softwood species, there is a significant correlation (reversed variation) between the average width of the growth layers and the wood's density, making it one of the parameters in use for the visual classification of the wood considering its mechanical resistance.

Sapwood and Heartwood

When a tree reaches a certain age, normally from between the 5th and 30th year of its life depending on the species, there is an onset of sapwood transforming into heartwood. This transformation, radiating from the central zone of the trunk, results from the cells' death and corresponds to chemical and physical changes. These represent the cessation of the transport of sap and the formation and deposition of residual products (extractives). Generally there is a change in the wood's colour (although in some species there is no chromatic distinction in between the heartwood and sapwood), a decrease in its permeability and, in most cases, an increase of the natural durability as well, as the products deposited on the heartwood may be repellent and toxic for the fungus and insects that degrade the wood.

Anisotropy

The tree's growth process results in an axial symmetry and a predominant direction of the cells that constitute the wood. This arrangement results in a marked anisotropy, both in the wood's mechanical and physical properties (shrinkage/swelling), and these are therefore commonly referred to as the different planes of the wood or directions given in Fig. 12.3.

The longitudinal direction is frequently designated by parallel direction to the fibres. The radial and tangential directions, both perpendicular to the fibres, correspond to any radius defined in the cross section and to any tangent to the growth layers, respectively.

Variability of the Wood

The great diversity of forest species being commercially exploited demonstrates the first factor of variability of the wood. This variation between species is particularly evident within the hardwood tree family ranging from pale, light, not very resistant nor durable wood, as is the case of balsa, to denser, darker, very resistant and durable wood, as is the case of Brazilian rosewood (palisander).

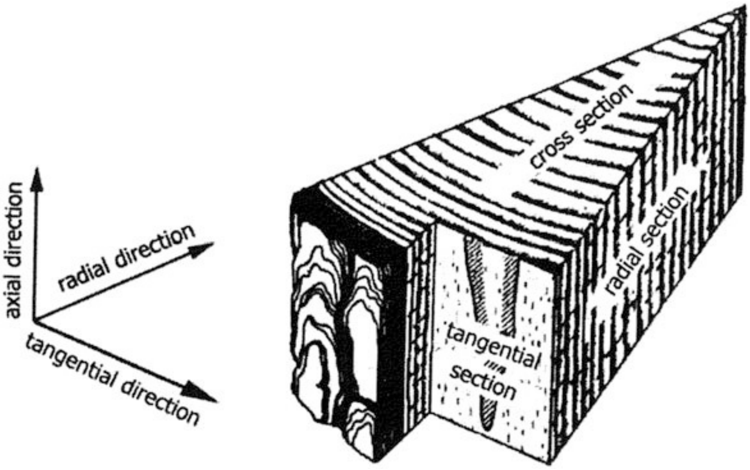

Fig. 12.3 Principal directions of wood [1]

It should be noted that the variation of the global wood marketing and distribution channels often places the buyer or user of wood in a position of complete unfamiliarity with what a particular wood species has to offer. Alongside this, new trade names are often used, more or less suggestive, that create confusion in the market because they hinder the demand for information or because they motivate the association with species of recognised potential, even if these have less durability or mechanical resistance. For this reason, the specification of a given wood, in addition to the trade name and geographical origin, should always include the botanical name (in Latin) of the forest species. The trade nomenclatures of forest species can be a valuable instrument in this regard, and they are included in publications and databases (e. g. reference [3]).

Factors such as climatic conditions, nature of the soil, water availability or type of forestry conduction also have an influence on the characteristics of the wood of a particular species. Some variation of the material within one same tree is also observed, usually denser near the periphery of the trunk and close to the base. Nevertheless, all these aspects are hardly verifiable at the time of the reception of the material so that the specification of the wood becomes inconclusive if based on these parameters.

On the other hand, the presence of certain particularities (defects, from the standpoint of the user) in wood, inherent to its natural origin, especially the knots, dilutes the intraspecies variability, such that it becomes the determining factor in the quality of the material.

Wood Defects

The quality of a piece of wood is measured by the average characteristics of the woody tissue and by the type, quantity and distribution of the defects it presents. A thorough description of the defects of wood can be found in the Portuguese Standard NP 180 [4]. The most significant characteristics and defects can be outlined as follows, considering the use in construction.

Knots – A knot corresponds to the portion of the base of a branch that grows out of the tree trunk. This shows a substantially conic development, radiating from the pith or somewhere near it. The knot shape in a piece of wood is, then, a function of orientation of the wood's cutting plane in relation to the branch.

The depreciative nature of the knots depends on the type of use—i.e. structural or nonstructural. For nonstructural uses, in which appearance is crucial, it is preferable to look for knots that are uniformly distributed, with little expression in the faces of the piece (small diameter), and that are sound and adherent. Further description can be found in the European Standard EN 942 [5].

The influence of the knots in the mechanical resistance of wood derives from the fact that they correspond to a material that is inserted in a piece, whose fibres are approximately perpendicular to the general direction of the fibres in that piece. Given the strong anisotropy of wood, resulting in a tensile strength about 30 times smaller in the direction perpendicular to the fibres than in the parallel direction, it is easily understood that, regardless of whether there are knots or groups of adherent knots, loose knots or knot holes, there is a minor contribution from the corresponding cross-section part. For this reason, for structural uses [6], the limits on knots or groups of knots are established in terms of the cross-section percentage of the piece they occupy, commonly known as KAR (knot area ratio) (Fig. 12.4).

Slope of grain – This is an anomaly reflected by the existence of an angle between the general direction of the wood fibres and the longitudinal axis of the piece. This may result from growth anomalies, such as the twisted grain, the curvature of the trunk or the oblique sawing of the pieces. Its consequences are

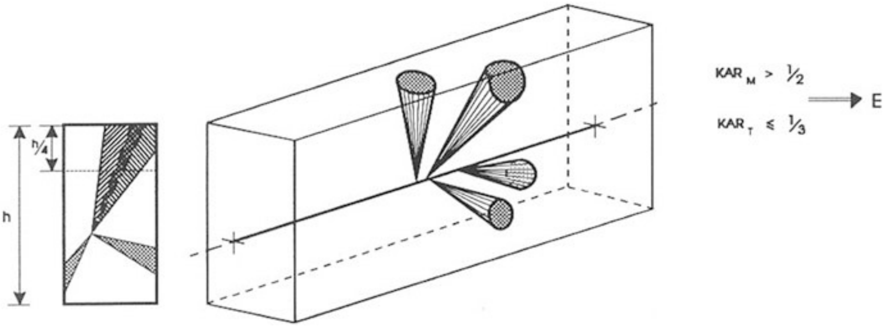

Fig. 12.4 Idealisation of the knots in the interior of a piece and evaluation of the total KAR and marginal KAR of a knot cluster [7]

linked once again with the material's anisotropy, for we move away from the ideal situation of applying the load parallel to the wood fibres.

Fissures – The presence of fissures introduces discontinuity in the wood material, and their effects on the wood's resistance depend on the type of stress considered, on their location, length and depth, as well as on the possible association with other defects such as knots or slope of grain.

Drying fissures develop in the same direction as the wood fibres, starting from the periphery of the trunk to the pith. Although there are certain types of wood that are most likely to split than others, the development of fissures is enhanced by sudden drying processes, with high gradients of moisture content in the cross section of the wood pieces, which is a processing defect.

Ring shake results from the detachment between consecutive growth layers, showing a circular development. They may occur in trees that are subject to frequent and excessive bending while they are growing, namely, under the action of strong winds or the effect of freezing.

Wane – Wane reflects the remainder of the torus surface in the wood piece, which is a processing defect. This presents particular difficulties with fixing, support and gluing, considering that the loss of resistance due to the reduction of the cross section is generally insignificant.

Growth rate – The growth rate is assessed by the average width of the annual growth rings. It is not a defect but is an important assessment parameter, particularly for softwood timbers. It reflects indirectly the wood density, which in its turn influences directly the wood strength and modulus of elasticity, but it is difficult to estimate in an expedient manner.

12.3 Hygroscopicity and Moisture Content

Wood Moisture and Shrinkage

Immediately after cutting down, all wood contains a large amount of water. Water is present in various forms: combined water, water of imbibition (or imbibition moisture) and free water.

Combined water is closely linked to the woody substance by powerful chemical sorption forces and cannot be removed without a chemical decomposition of the wood.

The water of imbibition fills the gaps between the constituents of the cell wall, by means of intermolecular attractive forces or infiltration by capillarity. Its release causes the approximation of the fibres and micelles, resulting in shrinkage of the wood and increasing its resistance and hardness.

On the other end, the free water fills the voids of the wood's honeycomb structure, having no connection whatsoever to the woody substance. Its movement inside the wood does not cause changes in its volume nor its mechanical resistance.

Following its cutting down, the wood loses its free water more or less rapidly. This process continues until all the free water has exited, while the cell walls still

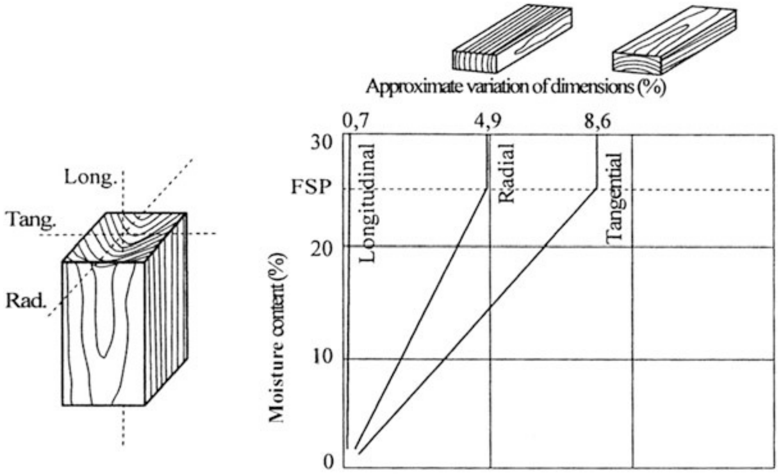

Fig. 12.5 Tangential, radial and longitudinal directions and their respective shrinkage coefficients in relative terms (averages for Maritime pine) [8]

maintain all their water of imbibition—corresponding to the fibre saturation point (FSP), which occurs at about 28–30 % moisture content, in most species. From its green state until this critical value, the wood does not suffer noticeable shrinkage or changes in mechanical resistance.

Later on, more slowly below the FSP, the wood will lose its water of imbibition, which is followed by more or less significant shrinkage, especially in the tangential and radial directions, as it is shown schematically in Fig. 12.5.

Dimensional Stability and Warp Formation

Below the FSP, shrinkage is approximately linear with the reduction of the wood's moisture content; this is a reversible phenomenon since the increase of moisture content will cause the wood to swell, approximately in equal measure. In reality the process is slightly hysteretic, where there is on average a differential of 2 % between the drying and rewetting curves, but it is ignored for simplicity.

It can be determined for each type of wood the shrinkage coefficients in the tangential, radial and axial directions, corresponding to the percentage variation in dimension (shrinkage or swelling) in that direction, which occurs for each variation in the wood's moisture content of 1 % in the range between 0 % and the FSP, usually being presented in %/%.

The dimensional variation in the axial or longitudinal direction Rl (parallel to the fibres) is, in practical terms, of little significance, being maximal in the tangential direction Rt.

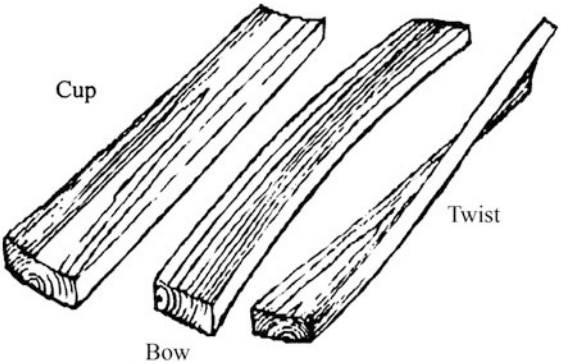

Fig. 12.6 Several types of warping (drawing by Tomás Mateus, cc 1960)

The shrinkage coefficients for a variety of wood species are contained in many publications and are an important factor to take into account in order to predict their behaviour after application, resulting in potential shrinkage, warping and fissures [9].

One way to classify wood, when it comes to its dimensional stability, is based on the factor of anisotropy, defined by the relation between the tangential and radial coefficients (Rt/Rr), which may vary between 1.5 and 2.5.

This classification derives from the fact that wood with a higher anisotropy factor usually has greater tendency to cup. The development of warping results from a distinct shrinkage on opposite faces, because one face has a greater predominance of tangential orientation when compared to the other (Fig. 12.6).

Warp in a wood piece, therefore, does not represent any loss of load carrying capacity. Despite this, it should still be regarded as a defect one should keep in mind when classifying wood, given that it will hinder use.

Moisture Content and Equilibrium Moisture Content

The moisture content of wood, H, at any given time, is defined by the following expression [8]:

$$H(\%) = \frac{\text{Wet mass} - \text{Dry mass}}{\text{Dry mass}} \times 100 \tag{12.1}$$

where wet mass is the initial mass of the wood sample and the dry mass of the same sample is obtained by drying at 103 ± 2 °C, until a constant mass is attained [10].

Wood is a hygroscopic material, varying its moisture content depending on the relative humidity and ambient air temperature. The absorption and desorption phenomena of water occur continuously, reaching the hygroscopic balance when these phenomena register the same rate. At this point, the wood has a moisture content said to be in equilibrium with the environmental conditions.

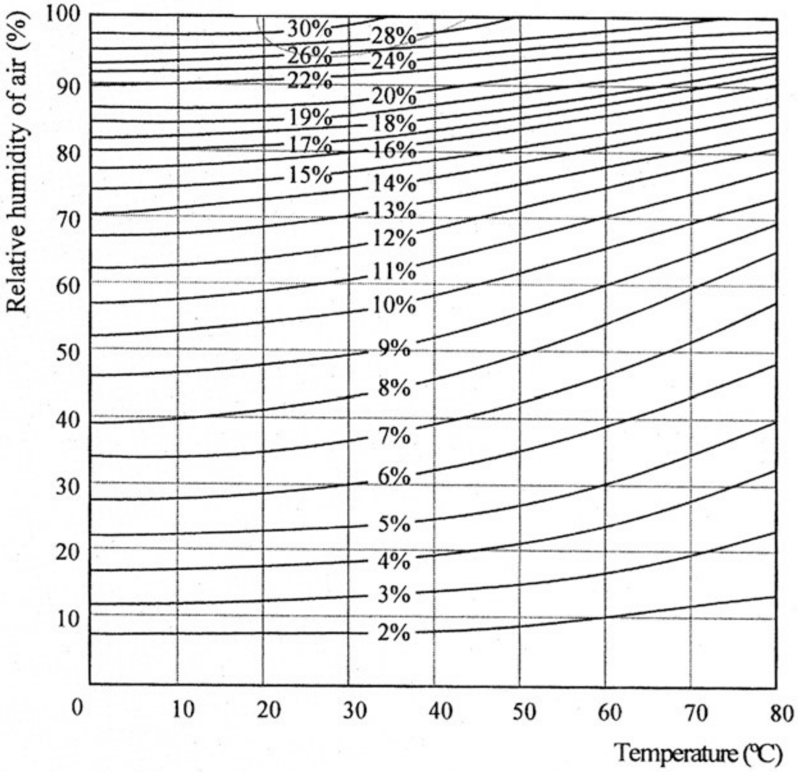

Fig. 12.7 Hygrometric equilibrium curves

Figure 12.7 shows the wood's equilibrium moisture content curves, obtained experimentally for the drying process of maritime pine, but they are generally applicable to other species. They allow for a prediction of the average equilibrium moisture content as well as the equilibrium moisture content that corresponds to extreme conditions of application (summer/winter or in construction/in operation).

The analysis of this figure also shows that wood drying in the open air will not normally allow the wood moisture content below 14–16 %. Besides these figures being a little too excessive for certain purposes or transformation processes, natural drying in drying stacks requires time and storage space.

On the other hand, industrial drying of wood in drying kilns makes it possible to reach values as low as desirable in a much faster way. The drying programmes to be used (temperature/humidity/time) in each case should be adjusted, not only to the final result that is intended but also to the species concerned, as well as to the quantity, dimensions and characteristics of the wood to be dried. This is a fundamental aspect, considering that an inadequate drying process may result in complete depreciation of the wood, due to the development of fissures and other major defects.

However, certain kinds of wood may require particularly slow and meticulous drying programmes, which will naturally raise the process costs. In these cases, it may be preferable to opt for a partial drying in the open air followed by a shorter period in the drying kilns.

Precautions for the Use of Wood

In order to minimise the wood's dimensional variations after the fabrication of building components or their application on site, it is essential that the wood is as close as possible to the equilibrium moisture content in relation to the site conditions.

The application of wood that is excessively wet may be just as inconvenient as the application of wood that is excessively dry, considering that both represent common deficiencies, e.g. in flooring applications. While in the first case it can cause opening of joints, fissures and warp, with eventual pull-out, in the second case it may cause the swelling of wood, possibly exceeding the capacity of the existing clearances and assembly joints to accommodate this dimensional increase that will usually lead to general displacement of the floor and introduce unacceptable stresses in surrounding elements, such as in wall plasters and baseboards.

For the same reason, situations of premature application of wood during building construction should be avoided, while screeds, mortars and plasters are insufficiently dried, which may contribute to the wetting of the wood, even if only temporary, but with the consequences described above.

Due to the effect that the moisture content has on the load bearing capacity of wood, it is also important to ensure that, when a structure comes into operation, the moisture content should not deviate significantly from the one which was considered in the structural design. The durability of wood can also be compromised if its moisture content is excessive at the time of construction (above 20–22 %), without this having been taken into account. Resistance and biological durability will be addressed later.

Specification and Verification of Moisture Content

The specification of the wood moisture content in the technical specifications must be defined objectively, indicating a reasonable range of variation or an average value, and the accepted tolerance (e.g. 14–16 %, or 12 ± 2 %).

Given the importance of this factor, it is necessary to foresee verification measures for the moisture content of the wood being used. Naturally, the collection of samples for laboratory drying in accordance with the standard EN 13183-1 [10] serves this purpose, and it is indeed the only rigorous method, even if there is various portable equipment for the expeditious assessment of the moisture content (contact wood moisture metres or wood moisture metres with needles) that allow immediate control of the material with minimum disturbance [8].

12.4 Load Carrying Capacity of Wood

Factors Influencing Wood Mechanical Properties

First of all, mechanical properties of wood are a function of the forest species and the quality of the wood piece which can be evaluated objectively considering the type and maximum size of defects. These two factors determine the characteristic values of density, elasticity and strength with respect to the various efforts.

Moreover, the load carrying capacity of a timber structure is also affected by its moisture content and by the load duration (load history). Timber strength is inversely proportional to its moisture content at each moment for values below the fibre saturation point (FSP) (Fig. 12.8(a)), and it is a reversible phenomenon. This should be taken into account, when designing the structure for both the ultimate limit states and for serviceability limit states as well as in the safety

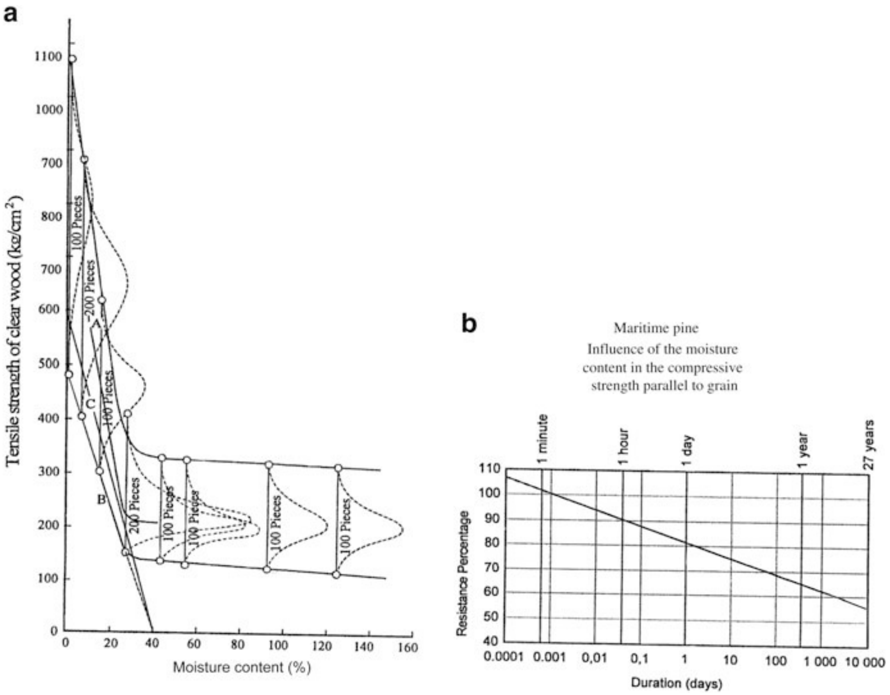

Fig. 12.8 (**a**) Relationship between moisture content and strength. (**b**) Relationship between load duration and strength

assessment during transitional situations, such as the assembly phase, during which the timber could possibly be exposed to rain [11].

The load duration reduces wood strength, according to Fig. 12.8(b), which means that the application of relatively high stresses, although below the material's strength, can damage the structure after a certain period of time. For the same reason, temporary structures should be designed to withstand higher stresses than in the case of permanent structures.

According to the Eurocode 5 [12], the moisture content of wood (i.e. the service class) and the duration of loads acting on the structure (i.e. the load duration class) are taken into account via a single modification factor, k_{mod}, which allows obtaining design values of the strength and stiffness properties from the corresponding characteristic values.

Mechanical Strength Sorting and Visual Strength Grading

Grading of wood allows for obtaining batches of material that are less varied, so that quality classes can be established based on mechanical strength criteria or aesthetic criteria. In both cases, each quality class is defined by a set of maximum values admitted for the different types of defects that have been visually evaluated.

Visual strength grading of structural timber has been a common practice in most developed countries, especially in Europe and North America, in some cases for more than half a century. The visual strength grading rules applied for this purpose vary from country to country, often based on traditional practice and adapted to the particularities of national species. For instance, the Portuguese standard NP 4305 [6] defines two visual strength grades for maritime pine timber (*Pinus pinaster* Ait.), established on the basis of maximum limits accepted for the following defects: knots (KAR), growth rate, slope of grain, fissures, pitch pockets or ingrown bark, presence of pith, wane and warp.

The European Committee for Standardisation (CEN), responsible for the elaboration of European standards, could not yet reach consensus on the establishment of a single European visual strength grading standard for structural timber, and therefore, each country continues to use their own rules in that respect.

Meanwhile, the characteristic values of mechanical strength, stiffness and density for these visual strength grades have been obtained through a large set of tests on pieces of structural dimension [7].

It is also possible to sort structural timber by using machine grading equipment, in which each board is subject to non-destructive tests (NDT) on relatively short sections, almost continuously. The piece's strength is automatically estimated from well-established correlations, for each forest species and dimension, between the bending strength and the properties assessed by the NDT. The machine grading of timber is a common practice in many countries, often interspersed in industrial production lines of structural elements or building products.

Visual Strength Grades and Strength Classes

The design of structures can be made assuming the use of timber of a certain species, source and strength grade, whose characteristic values of mechanical properties are well known. However, this procedure implies the prior choice of timber that is to be employed, and it can be restrictive in case the real market offer leads, later on, to the preferences of other forest species.

To overcome this limitation, the European Standard EN 338 [13] establishes two sets of strength classes for structural timber (one for softwoods and poplar and the other for hardwoods), each strength class being defined by a set of characteristic strength values, modulus of elasticity and density. Structural design can thus be made for a certain strength class, without the need to identify the species to be used.

The allocation to the strength classes established in EN 338 of the various combinations of species/source/grades of timber is established in EN 1912 [14], which indicates the different options that satisfy each of those strength classes.

Characteristic Strength Values and Design Strength Values

According to Eurocode 5, the design strength values of timber (f_d) to consider for verification of structural safety are derived from the corresponding characteristic values (f_k), by the following expression:

$$f_d = \frac{f_k}{\gamma_m}.k_{\text{mod}} \tag{12.2}$$

where:

γ_m—partial safety factor for timber, which is 1.3 for the verification of safety to the ultimate limit states, in the key combinations.

k_{mod}—modification factor which takes into account the service class (moisture content of wood) and the load duration class (duration of the action of the shortest duration included in the combination for which one is checking the safety of the structure).

12.5 Wood Deterioration by Physical and Chemical Agents

Wood is likely to deteriorate mainly due to biological agents, particularly fungi and insects; this happens also due to the action of fire or mechanical actions, such as wear, and on a smaller scale due to weathering and certain chemical actions as well. Wood is regarded as a material that is very resistant to a wide range of chemical environments. This behaviour makes it recommendable for harsh situations or environments with high exposure to chemical degradation, such as interior pools or other similar structures with minimum maintenance.

Weathering

With regard to weathering, sunlight—especially the radiation in the UV range—causes the chemical decomposition of lignin. Initially, this results in the darkening of wood (intensifying its characteristic colour) and subsequently the gradual shift to a grey tint which is often associated with 'old' wood (Fig. 12.9).

This process can, of course, be accelerated if there is, in addition to an intense sun exposure, direct impact of rain which removes the deteriorated material and progressively exposes the wood. In any case, the type of degradation caused by weathering is very slow, therefore affecting the wood mainly from an aesthetic point of view. The removal of this external layer, with 1–2 mm in depth, is usually enough to find the characteristic colour of the underlying wood, with all its original properties.

The application of coatings, such as paints, varnishes and wood stains, may slow this effect by reflecting or absorbing ultraviolet radiation, as well as having a repellent action to water [15].

The exposure to major environmental changes with dramatic alternations between drying and wetting can also cause development of fissures and warp, which constitute also a cause for deterioration, even if in most cases it is without major consequences for the mechanical strength.

Fire

From the point of view of the reaction to fire, wood has a poor performance. It is a combustible material, feeds combustion and is consumed by fire. This does not prevent some timber structures from having good fire resistance.

In a fire situation, the wood begins to dry by effect of temperature. The carbonisation of wood begins at about 280–300 °C, starting from the faces exposed

Fig. 12.9 Maritime pine wood showing the typical colour due to weathering

to the fire. The char that is formed remains adhered to the element, and because it is a good thermal insulator (superior to wood, which is already a good insulator), it helps delaying the rise in temperature of the underlying material. For that reason, it may happen that the temperature of the outer surface of the timber is insufficient to promote the progress of charring, thus leading to the self-extinguishing combustion.

The part of the Eurocode 5 that concerns structural design with regard to the action of fire [16] assumes a constant charring rate over time, between 0.5 mm and 0.8 mm per minute (depending on the type and density of the wood), which gives an average of about 1 cm progress of the charring front, from the exposed faces, every 15 min.

This explains why the fire resistance of a timber structure strongly depends on its specific surface area. Structural members of large cross sections of solid or glue-laminated wood are likely to present high fire resistance, while elements with a small cross section will present poor performance.

Slightly below the charred layer, the properties of non-charred wood suffered no significant change, so it may continue to perform its functions. This feature allows for a close account of the resistance of a timber structure during and after a fire situation. It also makes it possible to guarantee a given fire resistance for the timber structures, through oversizing the cross sections of the timber elements, complemented with the appropriate protection of structural joints.

In situations where this approach is not possible, particularly when improvement of the fire resistance for existing structures is intended, other solutions can be considered; passive protection of wood by coating materials or by affixing elements with low reaction to fire, e.g. based on plaster, or the painting of wood with appropriate products, are all valid options. The inks or varnishes for passive fire protection are normally intumescent products which react under the action of temperature, acting as the timber's thermal insulation, therefore delaying the beginning of charring.

12.6 Wood Deterioration by Biological Agents

Wood is used in many different exposure situations, particularly with respect to hygrothermal environmental conditions that affect the type and speed of material degradation by biological agents.

The moisture content of wood is therefore at the base of the use classes of application laid down in EN 335 [17]. The probability of deterioration depends not only on the biological agents known but also on the location of the piece of wood being used in construction. In addition to these factors, the service life of the material is also linked to its natural durability, understood as the natural resistance of wood to the attacks by living organisms (fungi, insects and marine borers) and to its impregnability, to the extent that it determines the viability of giving it added protection.

If the use class is correctly estimated (Table 12.1) and if the wood is properly prepared and utilised, being subjected to preservative treatment when necessary, the likelihood of severe cases of biological degradation is very low, whether caused by fungi or termites or by woodworms.

Table 12.1 Use classes for the application of solid wood (adapted from EN 335 [17])

Use class	General service situation	Description of exposure to wetting in service (wood moisture content in %)	Occurrence of biological agents (geographical variations are possible)
1	Interior, covered	Dry 20 % maximum	Beetles
			Termites
2	Interior, or under cover, not exposed to the weather. Possibility of water condensation	Occasionally >20 %	Beetles
			Termites
			Disfiguring fungi
			Brown rot
3	Exterior, above ground, exposed to the weather	Occasionally or frequently >20 %	Beetles
			Termites
	3.1 Limited wetting conditions		Blue stain fungi
	3.2 Prolonged wetting conditions		Brown rot
			White rot
4	Exterior in ground and/or fresh water	Predominantly or permanently >20 %	Beetles
			Termites
			Blue stain fungi
			Brown rot
			White rot
			Soft rot
5	In salt water	Permanently >20 %	Marine borers (=UC4, for elements outside the water)

Fungi

Due to its nature, wood is exposed to risks from biological degradation over time and environmental factors. This is true whether considering fungal attack by lignivorous agents on timbers of limited natural durability in the growing tree or in the sawn product, given the presence of optimum conditions for decay (Fig. 12.10).

It is common to distinguish the fungi that cause stains on the sapwood from those that cause the various types of wood rot (sapwood and heartwood). Among the latter, one should also consider the so-called microfungi, which cause soft rot (imperfect fungi and some ascomycetes), while the remaining cause the most frequent rots, such as white and brown rot (basidiomycetes fungi).

In general, fungal infections of the wood can easily occur and the attack begins as soon as the ecological conditions required for their development are established. They may result from the direct contamination by pieces already degraded or from spore germination in damp wood, carried by the wind or insects, in the cutting tools, etc.

Relative humidity conditions and the temperature of the environment in which wood is applied play a key role in the development of fungi. Low humidity will not

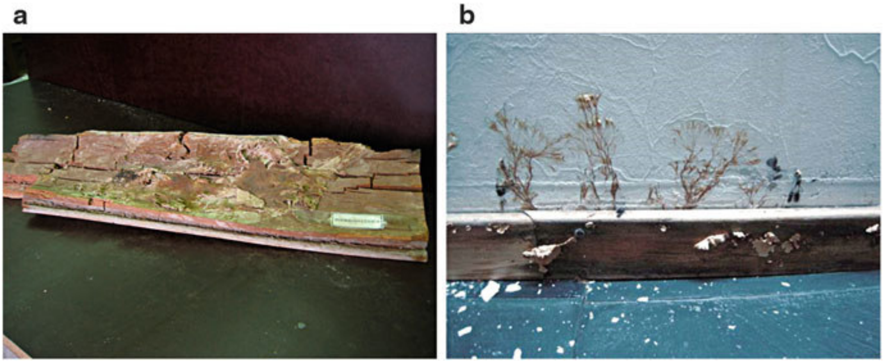

Fig. 12.10 (**a**) and (**b**) Appearance of fungal decay (rot) on a skirting board. Note the presence of fruiting bodies (mushrooms)

allow their progression, even in cases where an accidental humidification situation could allow for an infection. The fungus attack, in fact, takes place only when the moisture content of the wood reaches prolonged periods of values higher than 20 %, that is, much higher values than those corresponding to the condition of 'drying in open air' reached by the timber when placed in a normal environment, which are of the order of 14–15 %.

Thus, the woodwork of buildings not exposed to weathering (beams, floors, roof structures, etc.) is not normally in a position in which they can come to be attacked by fungi, unless there is contact with other building elements that receive water through capillary action. That cannot be said about the elements located outdoors (porches, windows and exterior doors), where conditions may often be favourable to the development of the fungi responsible for rot.

To be able to degrade wood and in addition to moisture, fungi also need suitable values of temperature and oxygen. The influence of these factors in the establishment, progression and severity of the attack depends on the infecting species, but generally speaking, it can be said that the growth of the fungi in wood takes place only with a moisture content above 22 % and at normal ambient temperature, which is situated between 10 and 30 °C, although they can withstand extreme values below and above this range. The absence of free oxygen by a complete saturation of the wood with water is a limiting factor in the development of these fungi, as is the application of temperatures above 40–50 °C or drying the wood for values under 20 %.

Subterranean Termites

The degradation of wood by the action of insects can be caused by different species with different modes of action and various signs of activity. Among the xylophagous insects, the action of subterranean termites is one that presents greater difficulties in diagnosis, given the scarcity of external symptoms of activity. Subterranean termites live in societies, organised in a caste system (colony), and the elements of each caste play a certain role in the colony (division of roles): reproductives, workers or soldiers.

The subterranean termites of the *Reticulitermes* genus (Isoptera, Rhinotermitidae) are widely diffused in Southern Europe [18], and since they feed primarily on cellulose, they occur in roots and stumps of trees and shrubs or in any other woody material in the soil, where there are favourable conditions for development, for which a highly humid environment is needed.

They usually circulate from their natural habitat to the constructions [18], where they may cause serious damage of the applied timber, provided that the conditions under which this material is lead to an abnormal elevation of its moisture. The damage that this insect causes in vulnerable timbers is extremely serious, not only by the volume of wood depredated but also by the fact that the attack happens inside the pieces, meaning that the destruction progresses without being detected.

Many timbers used in construction, particularly pine, are susceptible to being attacked by *R. grassei*. In the case of imported forest species, particularly tropical ones, the heartwood is sometimes resistant to attacks by this insect; therefore, infestations can be prevented when this wood is used in construction.

When present, the identification of this xylophagous agent is possible through the laminated appearance of the wood, which results from the destruction of the earlywood, while the latewood remains not substantially damaged (Fig. 12.11).

The most common outward signs of attack are mud tunnels constructed along the walls or pending from the rafters, through which the termites move, in their search for food, always protected from the light and whose detection is sufficient to identify the infestation (Fig. 12.12).

Fig. 12.11 Laminated appearance of the wood and the presence of mud tunnels resulting from the action of subterranean termites

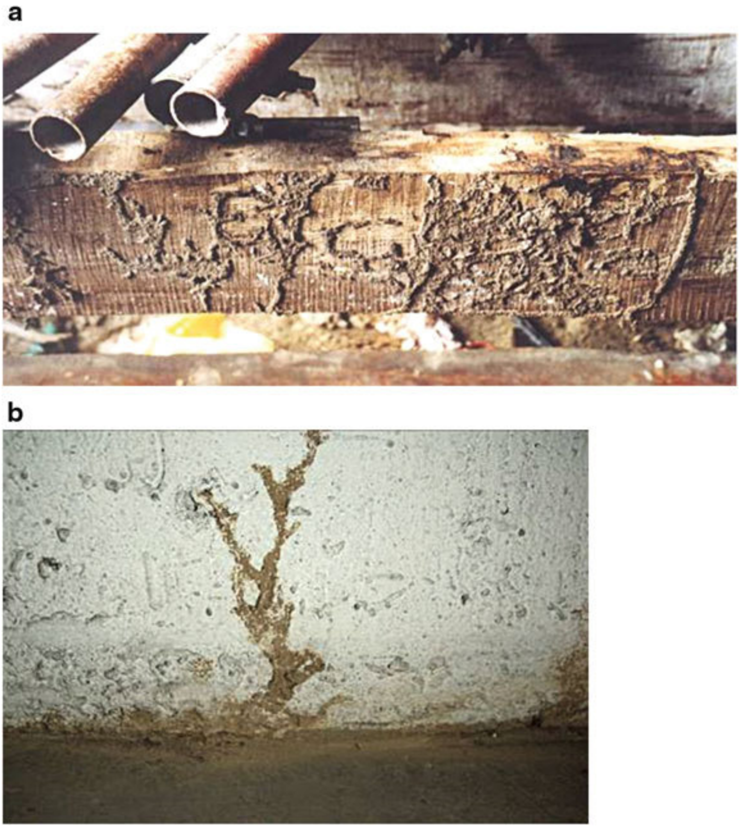

Fig. 12.12 Mud tunnels on timber (**a**) and on a brick wall (**b**)

There may also appear galleries and open spaces without sawdust but with mud concretions of characteristic feature, sometimes similar to combs in the wood's contact zones with the brickwork or within bricks. Another clear sign of a termite infestation is the presence of wings shedded immediately after the dispersion flights that occur every spring.

Insects of Dry Wood

With regard to insects with complete larval cycle, commonly referred to as woodworms, there are three important species: *Hylotrupes bajulus* L. (Coleoptera, Cerambycidae) known by the common name of house longhorn beetle, and there have been numerous records of its presence in constructions, particularly in structural timbers, roofs and floors; the *Anobium punctatum* (De Geer) (Coleoptera, Anobiidae) also known as common furniture beetle that is associated with structural timbers, roofs and floors and furniture in particular; and the *Lyctus* sp. (Coleoptera, Lyctidae), the powder post beetles, exclusively in hardwoods that are rich in starch.

It is possible to find in some European countries, but more particularly in the islands of Madeira and in some islands of the Azores, dry wood termite species that share some typical characteristics of an attack by woodworms but usually of a much greater severity (Isoptera, Kalotermitidae), with special reference to the species *Cryptotermes brevis* (Walker) [19].

In Table 12.2 and in Fig. 12.13, some characteristics of the infestations of dry wood, caused by woodworms and termites, are presented.

Table 12.2 Insects of dry wood. Some identifying characteristics of the attack

		Characteristic symptoms		
Insect	Wood	Holes	Bore dust	Others
Cerambicidae (e.g. *Hylotrupes bajulus*)	Softwoods	Emergence holes Oval 6–10 mm	Cream-coloured, sausage-shaped pellets. Small chips and wood fibres may be present. Dust-filled tunnels may cause blisters or corrugations on the surface of wood	Larval feeding may be audible as scraping noise
Anobidae (e.g. *Anobium punctatum*)	Softwoods and hardwoods	Emergence holes Circular 1–3 mm	Cream-coloured, lemon-shaped pellets. May accumulate in small piles beneath emergence holes	Frequent in older furniture and in constructional timbers in areas affected by damp
Lictidae (e.g. *Lyctus brunneus*)	Hardwoods with high starch content	Emergence holes Circular 1–2 mm	Cream-coloured. Fine, talk-like when rubbed between fingers. May accumulate in small piles beneath emergence holes	Bore dust easily shaken out of tunnels
Kalotermitidae (e.g. *Cryptotermes brevis*)	Softwoods and hardwoods	“Kick-out” holes Circular 1–3 mm	Pellets with six longitudinal surfaces, vary in colour from cream to black and are expelled periodically from different “kick-out” holes communicating with the gallery system. Very gritty when rubbed between fingers	Pellets will accumulate in piles directly beneath the holes. Pile diameter is proportional to the height from which pellets fall

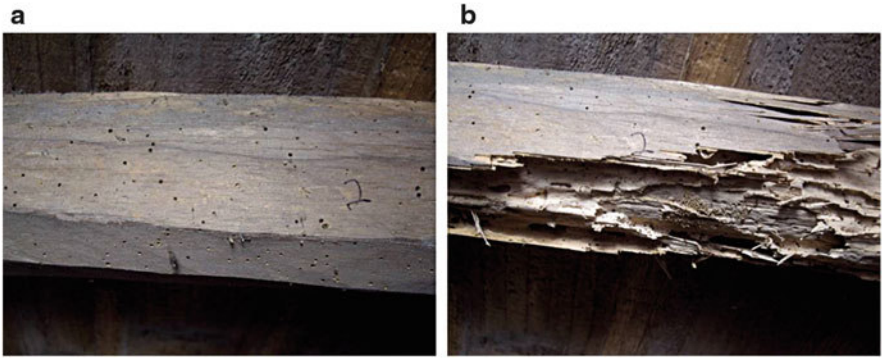

Fig. 12.13 Detail of an eucalyptus beam infected by dry wood termites, before (**a**) and after (**b**) the removal of the non-degraded surface wood layer

12.7 Conservation and Protection of Wood

Wood is a material with a long tradition of application in construction, but, because of its characteristics, it is subject to the risk of degradation by various biological agents.

When using wood for construction, the most important factor in their conservation is the preventive action. This implies a correct estimation of the risks to which the wood will be exposed to and a definition of the most suitable species in terms of natural durability in the service conditions. A number of protective measures that may protect the wood from predictable infections and infestations should be taken as well.

These measures are essentially of two types: (1) those that reduce or eliminate the probability of attack by placing the timber under natural conditions that prevent the establishment and development of biological agents, particularly important in the case of rot fungi and termites, where the wood's moisture content is the primary factor, and (2) those that prevent the development of the infestation or infection by means of chemicals and/or modification, either by treating the wood and/or masonry and surrounding soil or by acting at a more specific level for the pest species, such as the use of traps for controlling subterranean termites.

The adoption of certain design features and proper maintenance of the construction can also have a decisive effect on the conservation of wood, at least in situations where they may be subject to humidification, especially on roofs, ground floors and near bathrooms and kitchens. Critical aspects are adequate insulation and ventilation of guarded spaces, collecting and draining of rainwater, detailing and conducting the trim on the facade and roof and careful execution and maintenance of water and sewerage networks.

Because the correct application of the material is so important, it is recommended that their specification is made with care and always backed up by existing normative documents.

Wood may be properly selected for the intended final environment according to the sequence presented below:

- Consider the performance required for the wooden element.
- Determine the use class for the situation in which the wooden element will be used and for the biological agents that threaten it [17].
- Assess whether the natural durability of the wood to be used is sufficient or whether a preservative treatment is required [20–22].
- Select, for the element, wood species that are more durable, or choose another solution (design or design specifications) or emerging protection techniques (e.g. chemical or thermal modification) or by conventional preservation methods.
- If a preservative treatment is required, choose an appropriate treatment taking into account the biological agents for which protection is required [23–25].

When it is not possible to predict with sufficient certainty the use class of an element in service, or when it is estimated that the different areas of the same element are in different risk situations, the decisions should be made based on the most severe use classes among the applicable.

Also with regard to security issues, it should be taken into account that when a wooden element is inaccessible or when its consequences of failure are particularly dangerous, it might be more appropriate to use a wood that is more durable or a higher treatment level than the one that is usually recommended for the use class that corresponds to this application situation.

When situations of degradation occur, the rehabilitation of constructions is necessary in order to sustain the progression of degradation of materials or structures and, on the other hand, to reset or enhance their performance, that is, their durability, strength and functionality features.

Regarding the first aspect, a passive approach may be sufficient consisting in repairing the defects in the construction that potentiate the deterioration of wood, or, on the contrary, some measures specifically directed against the agent of deterioration (curative treatments) may be essential.

Any treatments that are selected for maintaining historical samples need to demonstrate that they do not result in any long-term alternative degradation risks, for example, through acidic decay. Thus, care must be taken when selecting any treatment; ensuring full assessments are carried out to ensure compatibility. This is particularly necessary with the application of new preservative treatment systems.

12.8 Wood-Based Products and Their Applications

Besides solid wood products, the use of wood in construction involves a growing number of wood-based materials [26]. These include: wood-based panels, namely, plywood, fibreboard and chipboard in all their variety, intended for uses that require large surface areas and small thickness, and materials that can be regarded as reconstituted solid timber, with the same type of use, in essence, as that of the solid wood, such as glue-laminated timber (glulam) and structural laminated veneer lumber (LVL).

Wood-based materials thus cover various families of products, with different manufacturing, properties and applications, in which the properties of the wood are blurred to some extent, compared to other manufacturing parameters. Therefore, they are subject to specific product standards, EN 312 (chipboard) [27], EN 622-1 (fibreboard) [28] and EN 636 (plywood) [29], which establish minimum requirements and support the selection of appropriate types of panels for the purpose wanted (structural or nonstructural, in a dry, humid or exterior environment), and also Parts 1, 2 and 3 of EN 12369 (characteristic strength values) [30–32].

Of these two, glue-laminated timber is undoubtedly the best known material. It is obtained by gluing face-to-face timber planks with about 3 to 4 cm in thickness, end-jointed by glued 'finger joints', and allows for straight or curved elements of any length and cross section. Synthetic glues of high mechanical strength are used, with good moisture resistance, high durability and good fire performance, since they resist temperatures that are close to that of wood charring. Technically, its production is very demanding and should be done by a careful quality control, as stated in EN 14080 [33].

All aspects above-mentioned in relation to solid wood apply equally to glue-laminated timber, including hygroscopicity and durability (mainly the function of the forest species used), the fire performance and also the influence of moisture and load duration (Eurocode 5 provides the same values of k_{mod} for solid or glue-laminated timber). In addition to the wood properties, the characteristics of the glue are also key features for mechanical performance and the durability of structures [34], considering that there are glues which are only suitable for dry indoor environments, bearing in mind that the quality of bonding also depends on the method and quality control of manufacture.

Although wood defects have the same kind of influence as on solid timber, in the case of glue-laminated beams, the production method results in a greater homogenisation (e.g. by dispersion of knots); therefore, there are specific grading rules for glulam lamellas and a distinct strength class system, established in EN 1194 [35].

With regard to structural laminated veneer lumber, its method of manufacture only allows for obtaining straight elements, so its application is common for 'I' shape plate girders used in temporary or permanent structures; there being also numerous examples of its use in skeletal structures of buildings of several floors or forming geodetic roofs. The material consists of wood sheets, in the order of 2 mm thickness, overlapped and bonded together to obtain the total thickness of the element; the orientation of the sheets is that of the axis of the structural elements to obtain, with a few sheets interspersed with the perpendicular orientation, to stabilise the assembly. Structural laminated veneer lumber partly reflects the physical properties and the durability of the wood used in its manufacture, presenting however greater dimensional stability, lower anisotropy and lower variability than solid wood, being covered by EN 14374 [36].

References

1. Machado JS, et al (2009) Madeira como Material Estrutural. In: Avaliação, Conservação e Reforço de Estruturas de Madeira. Verlag Dashöfer, Lisbon: pp. 5–22
2. Forest Products Laboratory (1999) Wood Handbook: Wood as an engineered material. Gen. Tech. Rep. FPL–GTR–113. United States Department of Agriculture, Madison, WI, p. 463
3. Machado JS (1996) Madeiras de Folhosas e Resinosas. Nomenclatura Comercial. ITES 11. LNEC, Lisbon, p 64
4. NP 180, Anomalias e Defeitos da Madeira. IPQ, Lisbon
5. EN 942, Timber in joinery—general classification of timber quality. CEN, Brussels
6. NP 4305, Madeira Serrada de Pinheiro Bravo para Estruturas—Classificação Visual. IPQ, Lisboa
7. LNEC (1997) Pinho bravo para estruturas.. Madeira para Construção—Ficha M2. Lisbon, LNEC
8. LNEC (1997) Humidade da madeira. Madeira para Construção – Ficha M9. Lisbon, LNEC
9. Carvalho A (1996) Madeiras Portuguesas. Vol.1: Estrutura Anatómica, Propriedades, Utilizações. Instituto Florestal. p. 340
10. EN 13183-1, Moisture content of a piece of sawn timber. Part 1: determination by oven dry method. CEN, Brussels
11. LNEC (1997) Especificação de Madeira para Estruturas. Madeira para Construção—Ficha M1. LNEC, Lisbon
12. EN 1995-1-1, Eurocode 5: design of timber structures. Part 1-1: general—common rules and rules for buildings. CEN, Brussels
13. EN 338, Structural timber—strength classes. CEN, Brussels
14. EN 1912, Structural timber: strength classes—assignment of visual grades and species. CEN, Brussels
15. LNEC (1997) Revestimentos por Pintura de Madeira para Exteriores. Madeira para Construção – Ficha M10. LNEC, Lisbon
16. EN 1995-1-2, Eurocode 5: design of timber structures. Part 1-2: general—structural fire design. CEN, Brussels
17. EN 335 (2013), Durability of wood and wood-based products. Use Classes: definitions, application to solid wood and wood-based products. CEN, Brussels
18. Nunes L (2008) Termite infestation risk in Portuguese historic buildings. Cost Action IE0601 «Wood Science for Conservation of Cultural Heritage». Braga, Portugal, 5 a 7 de Novembro de 2008. Online http://www.woodculther.org/
19. Nunes L et al (2010) First records of urban invasive Cryptotermes brevis (Isoptera: Kalotermitidae) in continental Spain and Portugal. J Appl Entomol 134:637–640. doi:10.1111/j.1439-0418.2009.01490.x
20. EN 350-1 , Durability of wood and wood-based products. Natural durability of solid wood. Part 1: guide to the principles of testing and classification of the natural durability of wood. CEN, Brussels
21. EN 350-2, Durability of wood and wood-based products. Natural durability of solid wood. Part 2: guide to natural durability and treatability of selected wood species of importance in Europe. CEN, Brussels
22. EN 460, Durability of wood and wood-based products. Natural durability of solid wood. Guide to the durability requirements for wood to be used in hazard classes. CEN, Brussels
23. EN 351-1, Durability of wood and wood-based products preservative-treated solid wood. Part 1: classification of preservative penetration and retention. CEN, Brussels
24. EN 351-2, Durability of wood and wood-based products. Preservative-treated solid wood. Part 2: guidance on sampling for the analysis of preservative-treated wood. CEN, Brussels
25. EN 599-1, Durability of wood and wood-based products. Efficacy of preventive wood preservatives as determined by biological tests. Part 1: specification according to use class. CEN, Brussels

26. Machado JS (2005) Placas de Derivados de Madeira. Tipos de Placas e sua Especificação. Informação Técnica de Estruturas, ITES 14. LNEC, Lisbon, p 96
27. EN 312, Particleboards. Specifications. CEN, Brussels
28. EN 622-1, Fibreboards. Specifications—Part 1: general requirements. CEN, Brussels
29. EN 636, Plywood. Specifications. CEN, Brussels
30. EN 12369-1, Wood-based panels. Characteristic values for structural design—part 1: OSB, particleboards and fibreboards. CEN, Brussels
31. EN 12369-2, Wood-based panels. Characteristic values for structural design—part 2: plywood. CEN, Brussels
32. EN 12369-3, Wood-based panels. Characteristic values for structural design—part 3: solid-wood panels. CEN, Brussels
33. EN 14080, Timber structures. Glued laminated timber and glued solid timber. Requirements. CEN, Brussels
34. Cruz H (2007) Estruturas de Madeira Lamelada colada em Portugal. Instrumentos para a Garantia da Qualidade. Revista Portuguesa de Engenharia de Estruturas, Série II 1:45–56
35. EN 1194, Timber structures. Glued laminated timber. Strength classes and determination of characteristic values. CEN, Brussels
36. EN 14374, Timber Structures. Structural Laminated Veneer Lumber. Requirements. CEN, Brussels

Cork

13

Luís Gil

Abstract

Cork is the bark of the cork oak. It is a light, elastic material that is practically impermeable to liquid and gas, as well as being a thermal and electrical insulator. It also absorbs sound and vibrations and practically impossible to rot. Cork is composed of layers of cells, whose membranes have a certain amount of impermeability and are full of a gas similar to air. When cork is compressed, its cells bend and fold (practically no lateral expansion) and later recover. Cork is also a material that dissipates deformation energy. It has low thermal conductivity and is also remarkably stable and has good fire resistance. The most common cork products for civil construction are: insulators against noise, heat and vibration (walls, ceilings, flooring); false ceilings; coverings for walls, floors and ceilings; skirting boards; linoleums; granulated cork as filler and mixtures for mortar; insulating joints and expansion or compression joints; and anti-vibration devices for machinery and insulation for industrial refrigeration systems. Cork products are also very important from an ecological standpoint, because cork is a renewable product, used in long-life products, helping to boost CO_2 sequestration.

Keywords

Cork • Cork products • Flooring • Insulation • Covering • Physical properties • Mechanical properties • Civil construction • Environment • Ecology

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M.C. Gonçalves, F. Margarido (eds.), *Materials for Construction and Civil Engineering*, DOI 10.1007/978-3-319-08236-3_13

13.1 Introduction

What Is Cork?

Cork is a material which is known to have been used since antiquity, above all as a floating and sealing material. Its market expanded enormously from the beginning of the twentieth century, specifically as a result of several agglomerated products based on cork. By definition, cork is a suberose parenchyma created by the cork cambium meristem of the cork oak (*Quercus suber* L.), forming the outer layer of its trunk and branches. At macroscopic level, it is a light, elastic material that is practically impermeable to liquid and gas, as well as being a thermal and electrical insulator. It also absorbs sound and vibrations and is safe and practically impossible to rot. It can be compressed without increasing in size at the sides. At microscopic level, cork is composed of layers of cells that are alveolar in aspect, whose cell membranes have a certain amount of impermeability and are full of a gas similar to air, which occupies 90 % of its volume [1].

When cork is compressed, its cells bend and fold, which means it has practically no lateral expansion and later recovers. Cork is also a material that dissipates deformation energy. Its average density is around 200 kg/m^3, and it has low thermal conductivity. Cork is also remarkably stable, both chemically and biologically, and has good fire resistance [1].

The European Union is the largest cork producer (more than 80 %) in the world. Its production is concentrated in the Western Mediterranean countries, of which Portugal stands out (more than 50 %) as the largest cork producer and processor. Cork oaks are extremely well adapted to southern Europe and North Africa, helping to avoid desertification and promoting carbon sink and other external factors. Cork oak forests are also the habitat of many unique plant and animal species [2].

Raw Materials of Cork

Cork is extracted from the trunk and branches of the cork oak, in semi-tubular form, normally in summer and at legally defined intervals of at least 9 years. It can be extracted once the tree has reached 0.7 m in perimeter and 1.3 m from the ground. The tree cannot be totally “stripped” of its suberose layer. The operation is carried out manually using axes, as demonstrated in Fig. 13.1, and there are already mechanical processes as well.

The first cork harvest yields a type of cork known as virgin cork (Fig. 13.2), which has a very uneven outer surface. Successive harvests produce cork with a more even surface, and this is known as reproduction or *amadia* cork (Fig. 13.2). The first batch of reproduction cork, which is still slightly uneven, is known as secondary cork and has similar uses as virgin cork (grinding → granulated cork → agglomerates). Chunks of cork (*falca*) are obtained from the offcuts, consisting of a mixture of virgin cork, phloem and xylem, and are traditionally

Fig. 13.1 Stripping the cork from a cork oak tree

Fig. 13.2 Virgin cork (*cortiça virgem*) and reproduction cork (*cortiça amadia*)

removed with an axe or adze from the branches pruned from the cork oaks or, more recently, using other specific equipment [1, 3].

In composition cork, granulated cork is obtained by grinding virgin cork, lumps, scraps and waste materials from processing operations, such as shavings (from drills, cutting, etc.), defective cork stoppers, material leftover from agglomerates, etc. When manufacturing expanded agglomerated cork, a more roughly ground cork is used, normally using a particle size in the 5–20 mm range, but which can reach up to 3–22 mm [4], obtained mostly by grinding virgin cork from pruned cork oak branches (*falca*) and other smaller types of cork (Fig. 13.3).

Fig. 13.3 *Falca*, chunks of wood from pruned branches of virgin cork

Manufacturing Cork Products for Civil Construction

Using Portuguese industry as a reference, recent data [5] show that in 2007 (considered as an average year) 94,700 tonnes of cork construction materials were exported by Portugal, divided into (numbers from the National Statistics Institute (INE)):

- 4501.90.00—cork waste, ground, granulated or pulverised cork (26,700 tonnes)
- 4504.10.91—cubes, blocks, sheets, strips, tiles and solid cylinders made of agglomerated cork with binding agents (28,800 tonnes)
- 4504.10.99—idem, without binding agents (26,600 tonnes)
- 4504.90.99—agglomerated cork and articles of agglomerated cork (12,500 tonnes)

The most common cork products for civil construction are insulators against noise, heat and vibration (walls, ceilings, flooring); false ceilings; coverings for walls, floors and ceilings; skirting boards; linoleums; granulated cork as fillers and mixtures for mortar; insulating joints and expansion or compression joints; industrial utilizations; anti-vibration devices for machinery; and insulation for industrial refrigeration systems.

A brief description of the manufacturing processes for cork products for civil construction will follow, and a full diagram is given in Fig. 13.4.

Granulated cork is obtained by using toothed mills (shredders), hammer mills and knife mills; attrition mills work essentially to adjust the particle size and to give

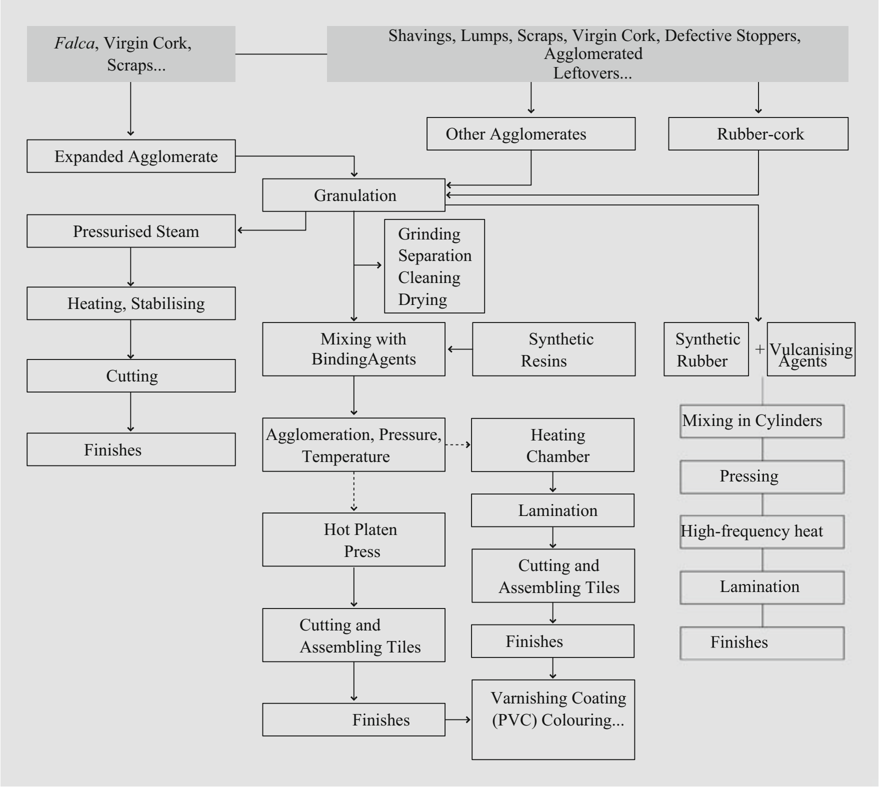

Fig. 13.4 Full diagram of the manufacturing process for cork construction products

the granules a final clean [6]. It is also dried using forced airflow to give the granulated material the desired moisture content.

Following the cork processing, using the granules (usually 2–6 mm), we find the production of composition cork, which is the result of a process of binding the granules using pressure, temperature and binding agent. After using an automatic dosing device or manual dosing device, the granules are mixed with the binding agents, usually through a mechanical process, using a rolling process in the case of "rubber-cork" [1].

For decorative purposes, for example, a density of between 200 and 350 kg/m^3 and fine–medium-sized granules are used. Expansion joints are manufactured using medium-sized granules and an average density of 250–350 kg/m^3 [1]. For agglomerates designed for use as floor coverings, density is normally greater than 450 kg/m^3 and may reach up to 600 kg/m^3.

Manufacturing this type of agglomerated cork mostly uses synthetic polyurethane, phenol-formaldehyde and melamine resins, but sometimes organic resins may also be used [6–8], and there are also binding agents based on enzymes.

The exact quantity of the mixture to be used is then measured and placed in moulds, usually made of metal and in the shape of a parallelepiped (when making stoppers, cylindrical moulds are used). Afterwards, lids of the same material are put on, and they are pressed, locked under a certain amount of pressure. The moulds containing the pressed mixture are placed in "curing" chambers (polymerisation of the binding agents). The "curing" chambers may be ovens or high-frequency systems.

In the first case, temperatures of 110–150 ºC are used for between 4 and 22 h [8, 9]. These two parameters should be enough for the glues to be polymerised. In the first case, the "curing" system may be continuous (in a tunnel) or discontinuous. In the second case (microwaves), the process is quite a lot quicker, as short as 3 or 4 min [6, 9].

After "curing", the cork is removed from the moulds and cooled/stabilised, until a block of agglomerate is formed, which is then laminated into sheets, sometimes using heat. For rolls of cork, the cylinders obtained are unrolled using continuous lamination, and the sheet is then rolled up.

The next stage is sanding the surface of the sheets to correct the thickness and achieve the level of roughness desired. The prepared sheets are then cut into the desired shape, usually square or rectangular tiles, and their dimensions and shape are corrected [1].

The different types of decorative and covering materials are obtained either with a single layer or by placing several different types of the agglomerated sheets or laminate natural cork on top of each other or by using composites formed with other materials, specifically wood or fibre agglomerates or wood particles. Gluing the successive layers together is performed by spreading glue on one of the sides of each sheet and passing the whole set through a press, usually a roll press or plate press [9].

The so-called laminate or floating flooring is usually made with an intermediate layer of MDF or HDF (medium- and high-density wood fibreboard, respectively), with a sheet of agglomerated cork on the lower side and a sheet of decorative cork on the upper side, and the whole thing is then glued and pressed. The MDF or HDF is cut using a milling machine to obtain a fitting system (such as a click-lock or tongue-and-groove system) [2].

The panels formed (either tiles or laminate boards) can then be given several different types of surface finishes on the cork: waxing, varnishing and coating with different types of film (e.g. PVC).

Synthetic (acrylic or polyurethane) or water-based varnishes are usually used if varnishing is chosen. Varnishes and agglomerates may also be coloured using pigment, with a range of colours available [1, 2]. The cure for varnishing is normally done using UV radiation or forced hot air tunnels. Some of the patterns for cork-tile finishes sold are shown in Fig. 13.5.

Some manufacturers also make a final selection of tiles by shade (manually or automatically). Further to this selection, there is also a final manual/visual selection/rejection to check for defects.

There is an agglomeration process for manufacturing composition cork that differs from the processes described here and which can be summarised as follows

Fig. 13.5 Examples of different patterns of cork flooring

[8, 9]: the mixture (granules + binding agents) with different particle sizes is distributed on a conveyor belt and placed in a large-scale plate press, thereby obtaining a single sheet, with operating parameters usually found within the following ranges: plate temperature, 120–180 °C; pressure applied, 5–15 daN/cm^2; and pressing time, 3–8 min [1].

Finer and denser granules are used for linoleum manufacturing and are mixed with oxidised linseed oil, resin, jute, sawdust, metal oxides and colouring to form a compact product that is highly resistant to wear and easy to clean, used mostly as a covering [1].

Another type of cork-based agglomerate, manufactured using a rather different production method and also used in some different areas, is commonly known as "rubber-cork" or "cork-rubber", that is, an agglomerate formed of cork and rubber. This type of agglomerate is used mostly for joints and flooring, above all in places with a lot of traffic [9]. The amount of rubber involved naturally depends on the use for which the agglomerate is designed. In its different forms, as well as cork and rubber granules, vulcanising agents, antioxidants, polymerisation accelerators, dyes, etc. are also used.

The manufacturing process can be summarised as follows: the mixture to be agglomerated, formed of granulated cork and rubber (either powdered or small particles) and other agents, is homogenised, compressed and heated in cylindrical mixers. The mixture is then passed through a calender to form a homogenous mass [10]. This pulp is then cut into panels and placed in moulds, pressed and cured, in the same way as normal composition cork [9], and the blocks that result are then cut up.

In the case of high-frequency "curing", the moulds are made out of synthetic resin strengthened with fibreglass [6]. High-frequency "curing" takes 10–12 min.

The expanded agglomerated cork industry uses cork that is not normally processed by other granulating/agglomerating industries. On the other hand, using raw virgin cork is positive, since it has a high level of extractives, which work as inter-granule binders.

The granulation stage, which includes grinding and cleaning, is similar to the process used for other types of agglomerated cork. The final grain size obtained depends on the agglomerate to be manufactured, but is generally 5–20 mm: 3–10 mm for acoustic agglomerates and 5–22 mm for thermal agglomerates. The following stage involves removing impurities, with the help of densimetric separators, sieves and, possibly, pneumatic separators or conveyor belts. The granulated cork that results is then stored in silos and dried until it has the right moisture levels for the "baking" stage [1].

The following stage, agglomeration, is carried out using an autoclave process (see Fig. 13.6). The granulated cork is loaded, and once the mould is closed, it is lightly pressed during the autoclave process, in which the mould is the autoclave itself. It is heated by injecting superheated steam, at an average temperature of 300–370 °C. The superheated steam is normally introduced through holes on the bottom

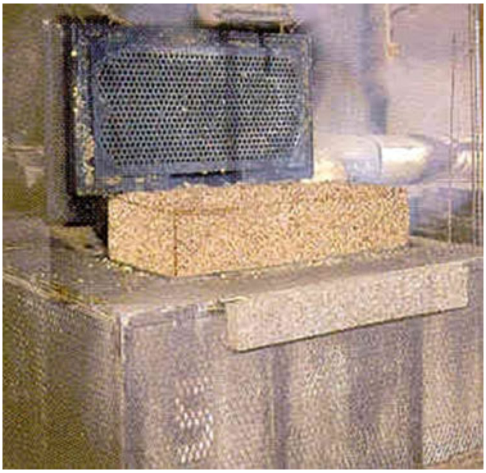

Fig. 13.6 Block of expanded agglomerated cork, coming out of the autoclave

Fig. 13.7 Cutting the block into boards

of the autoclave, passing through the mass of granules and producing exudation of the remaining cork resins to the surface of the granules, increasing their volume and causing binding to occur. Baking time is 17–30 min in most cases [1].

The blocks produced are cut into panels of different thicknesses, as seen in Fig. 13.7, and the dimensions are corrected normally using circular saws and sanders.

The rejected (uneven) upper and lower parts of the blocks or defective panels or those obtained from demolitions are used to make regranulated expanded cork, through regrinding.

13.2 Structure and Composition of Cork

Macroscopic Structure of Cork

When the cork is extracted from the trees, the external part of the phloem is exposed, which is then "pushed" by successive layers of new cells that are formed inside. This produces the outer bark, which constitutes the outermost part of the cork. This layer dries, contracts and hardens, cracking due to the increase in the outer perimeter in comparison with the inner perimeter because of growth. Likewise, the inner part of the suberose matter is the last layer of annual growth. It has less elasticity than the other layers and has lenticels (pores). Porosity is closely linked to the quality of the cork [1, 3].

Virgin cork does not have an outer bark. Throughout the width of the cork, growth rings can be seen, distinguishable, because they are formed of cells with cell walls of different sizes and different thicknesses formed in spring/summer or autumn/winter. For example, a 9-year-old cork has nine complete autumn layers, eight complete spring layers and two half-spring layers: one next to the outer bark, immediately following the previous cork harvest, and another next to the innermost layer, which was in the process of being formed at the time of peeling. From a practical standpoint, all that is needed is to count the dark autumn layers, if they are markedly different, to find out how many years old the cork is [2].

There are some aspects that are normally considered indicators of the quality of cork: a light colour for virgin cork and the flatness, softness and thinness of the back of reproduction cork. Ultimately, the quality of the cork is determined by the homogeneity of the mass of suberose cells in relation to discontinuities or external matter that is found in between. Among these discontinuities there are always lenticular channels that cross the cork outwards, giving rise to pores transversally. The type, size, quantity and distribution of pores are also determining factors in the quality of cork [1].

There is a variety of structural and other defects in cork (e.g. yellow stains, insects, etc.) that are only important for use as stoppers and not for construction.

The structure of cork is anisotropic. The main directions for cork are radial (parallel to the roots of the tree), axial (vertically up and down the tree) and tangential (at right angles to the other two, tangent to the circumference of the section of the tree). The perpendicular sections of these three directions are called tangential, transversal and radial, respectively [11]. However, anisotropy is not found in agglomerated cork, which is used for cork construction products, because of the random distribution/orientation of the granules.

Microscopic Structure of Cork

Cork is a tissue consisting of cell membranes whose content disappeared during growth and that later undergo a suberification process. It is not just the structure of the tissue that gives cork its characteristics, since many of its properties are due to the nature of the cell membranes. Communication between cells is ensured by microchannels that pass through the cell wall and are known as plasmodesmata. Cork consists of cells (see Fig. 13.8) that are compacted together without free space and evenly distributed. Cell walls form around 10–15 % of the total volume [1].

The cell walls are formed of a structural base of suberin and polymeric polyphenols, like lignin, with a high quantity of extractable wax. Cork cell walls have five layers: two are cellulosic, which line the cell cavities; two layers further in which are suberose (providing impermeability); and a middle lignified layer (providing rigidity and structure). The suberose layers show alternate layers of suberin and wax [1].

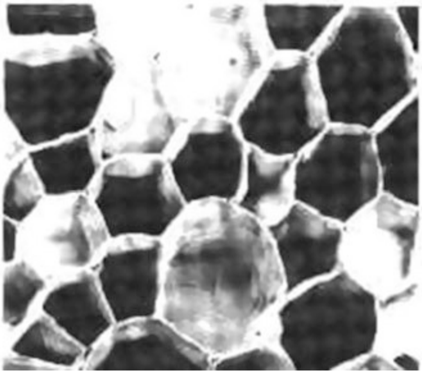

Fig. 13.8 Cork cells

The cell membranes are thinner in cells produced in spring and summer (1–1.25 μm) and greater in autumn and winter (2–2.5 μm). This fact, linked with the larger or smaller size of cells, changes the physical and mechanical properties of the cork. This is why fast-growing cork with thicker suberose rings are less dense, more compressive and less elastic than thinner cork [1].

It can be said that an average cork cell could be represented by a hexagonal prism, with the number of sides normally between 4 and 9, but preferably between 5 and 7. Its average dimensions are between 30 and 40 μm wide (up to 10 and 50 μm) and 35 and 45 μm high, with limits between 10 and 70 μm.

1 cm^3 of cork has between 30 and 42 million cells on average, depending on whether it is a fast- or slow-growing sample. Each annual ring normally includes 50–200 cells measuring 1–6 mm in width, and this variation is the main reason for the different thicknesses in annual cork growth.

As has been mentioned, the differences in the size of the cells and the thickness of their walls, between those formed in autumn and spring, make the rings of cork formed each year visible, as the cells formed in autumn (smaller and thicker) have a darker colour [1, 11].

The cork's insulation characteristics are due to the fact that there are minuscule compartments (cells) filled with air. The cork cells are much smaller than an ordinary cell matter, which helps to explain this material's exceptional insulation properties. Heat transfer through conduction depends only on the quantity of solid material in the cell structure (which is less for thermally expanded cork). Convection depends on the size of the cells and does not contribute notably for small cells. Radiation also depends on the size of the cells: the smaller they are, the more times the heat has to be absorbed and reradiated [1].

Chemical Composition of Cork

The chemical composition of cork includes several types of compounds, which are traditionally divided into five groups. The amounts are roughly as follows: suberin (45 %, main constituent and responsible for compressibility and elasticity), lignin (27 %, cell wall structure), polysaccharides (12 %, also linked to the cork's structure), wax (6 %, repels water and helps maintain impermeability), tannins (6 %, material protection) and ash (4 %) [1].

Reproduction (secondary and mature) cork has a material in its outer layer, the outer bark, which virgin cork does not. This material has a notably different composition comparing to the suberose material. The composition is as follows: ash, 9.8 %; extractives, 8 %; suberin, 4.3 %; insoluble lignin, 30.9 %; soluble lignin, 1.6 %; and polysaccharides, 40.3 % [1].

Therefore, cork consists of complex, long polymeric structural components and nonstructural components. The latter can be divided into extractive and non-extractive components. The former are obtained and separated without deterioration, and the latter consist of inorganic substances that form ash and nitrogen compounds, such as proteins. The extractives can be divided into waxes, which influence cork's impermeability properties, and phenolic compounds, which appear to protect the cork against attacks by biological organisms [1].

13.3 Cork Products and Their Physical and Mechanical Characteristics

Agglomerated Cork for Coverings (Floors and Walls)

Currently, cork flooring is becoming more and more recognised for its advantageous technical properties and the fact that it also has a pleasant appearance. A few years ago it may have been considered out of fashion, but it has recently become a favoured product in the world of interior design in some important markets. Some natural flooring is linked with noise problems and sometimes produces cold environments, situations that are completely overcome by using cork products [12]. In terms of cork's performance as a floor covering, it would be interesting to consider the following explanations:

Friction between the shoes and the floor arises from two factors. One is adhesion, as atomic links are formed between the two surfaces in contact, and an effort must be made to break and reform those links if the shoe slips. This effect is the only one that takes place, for example, between a hard sole and a stone floor, and since it is only a surface effect, it is cancelled out by polishing, for instance. The other factor is due to inelastic loss. When the sole slips on a cork floor, it deforms it.

If the cork was perfectly elastic, it would not be necessary to exert effort, since what was lost at the beginning would be recovered afterwards. However, since cork has a high energy dissipation rate, it is like riding a bike in the sand: the effort made is not recovered. This effect (antislip) is the main one when rough surfaces slide over cork, and as it depends on processes that take place under the surface, it is not affected by film, polishing or washing. The same thing happens when a cylinder or sphere rolls over the cork [1]. Besides these properties relating to friction, cork is resilient and absorbs the shocks from motion (impact noise), providing comfort.

Cork's resilience means that cork coverings relieve tension in joints and in the spine and are pleasant to touch. Since they are poor thermal conductors, they feel warm to touch, which is important in certain cultures, and they do not get dirty easily. They also reduce noise from the impact of walking [2].

Cork parquet flooring tiles have a density of around 450–500 kg/m^3 and a heat transfer coefficient of 0.06–0.10 W/m K. The most common dimensions are 300 × 300 mm, 600 × 300 mm, 900 × 300 mm and 900 × 150 mm with thicknesses of between 3.2 and 8 mm [2].

Studies carried out on a series of commercially available products made it possible to find the amount of formaldehyde released, which varied between 0.036 and 33.86 mg/kg of dry sample, below the maximum permitted ($\leq$95 mg/kg of dry sample), in accordance with standard EN 12781 [2]. The values presented by manufacturers for the tensile strength of cork parquet flooring are 0.15–0.20 MPa.

The figures obtained for insulation of a solid reinforced metal slab with 250 kg/m^2, relating to the index of impact noise insulation (L, low; M, medium; H, high) for different ranges, using different cork coverings, were [13]:

- Composition cork, 570 kg/m^3, 5 mm: IL = 0 dB; IM = 4 dB; IH = 34 dB
- Composition cork, 503 kg/m^3, 5 mm: IL = 0 dB; IM = 4 dB; IH = 40 dB
- Composition cork, 400 kg/m^3, 6 mm: IL = 0 dB; IM = 11 dB; IH = 47 dB
- Composition cork, 490 kg/m^3, 12 mm: IL = 0 dB; IM = 13 dB; IH = 41 dB

Again for parquet-type agglomerated cork, studies on size stability in atmospheres with different relative air humidity were carried out, concluding that variation was less than 1 % [14, 15].

Soft agglomerated cork material with densities in the 200–300 kg/m^3 range have a dimensional variation with humidity in the same order as parquet flooring, a tensile strength of around 0.2–1.2 MPa and a thermal conductivity coefficient of 0.061–0.064 W/m K ([1] and manufacturers' catalogues).

The oxygen index (flammability) of several types of soft, decorative composition cork agglomerate was tested, with results always between 20.5 and 21 %. Cork parquet, whether normal or with PVC, gave higher results, around 26.5–27 % [16]. The higher the results, the lower the flammability.

The water vapour permeability for a composition cork of 480 kg/m^3 was 0.0002 g/m h mmHg [17].

Laminate flooring (see Fig. 13.9) normally consists of an agglomerated cork base measuring 1–3 mm; an intermediate layer of MDF or HDF, 6–7 mm; and a "usage" layer made of cork, 2.5–3.2 mm thick, giving rise to a total thickness of 10–12 mm and linear dimensions of 900 × 300 mm, with tongue-and-groove connections for gluing or click-lock systems [2].

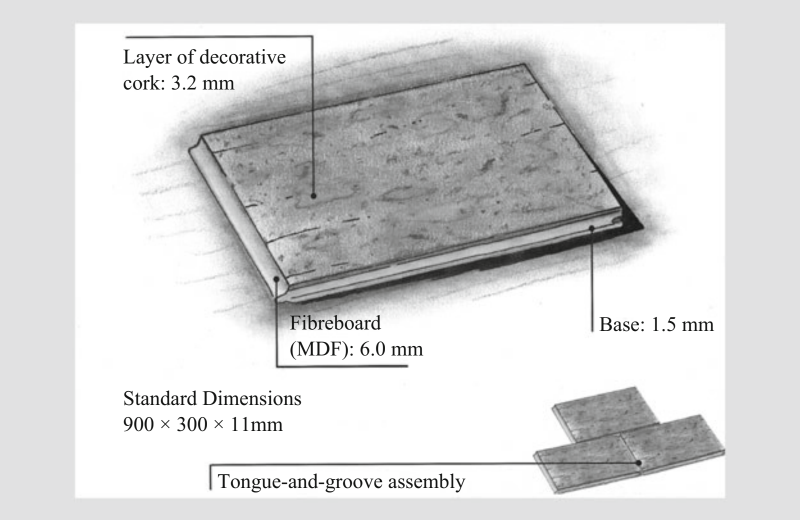

Fig. 13.9 Diagram showing cork laminate flooring

The durability of cork coverings is widely recognised, provided that it is appropriately maintained by periodically renewing the protection products. Some known cases of proven durability are [2]:

- The cork flooring at the Escuela Técnica Superior de Ingenieros de Montes, in Madrid, which had a very intensive use, was laid in the 1950s and was still in place in the 1990s.
- In 2007 there were still some wings of the Santa Maria Hospital in Lisbon (extremely intensive use) where cork coverings have been in use for decades.
- Many buildings in Lisbon from the 1940s and 1950s all around the city (but above all in *Lapa* and *Avenidas Novas*) still have their original coverings, flooring and panelling.

Agglomerated Cork for Sound and Thermal Insulation

In this area, we have the thermal insulation of buildings (see characteristics in Table 13.1)—ceiling, floors and walls—protecting reinforced concrete coverings against temperature variations, reducing energy loss, protecting slabs and, furthermore, stopping or reducing surface condensation on walls and ceilings. In terms of noise (see characteristics in Table 13.2), we have sound correction through noise absorption and a reduction in reverberation time in certain settings and also through a reduction of impact noise in special uses [1, 18].

Another specific case of thermal insulation for which the densest expanded agglomerates are used is insulation for refrigeration facilities in areas where high fixed or mobile pressure is exerted, specifically in loading/unloading areas [2].

In terms of impact, expanded agglomerated cork may be used in a layer between the lining and the flooring itself (laminate flooring). Wall and ceiling coverings absorb part of the total sound energy, reducing the intensity of the reflected sound. An uneven surface, with cavities, also helps by increasing sound reflection and energy lost in each reflection [2].

The thermal conductivity (λ) of a thermal-type expanded agglomerated cork varies in line with the average (T_m) temperature (–150 to 50 °C) of the test and with density (ρ) according to this formula [19]:

$$\begin{aligned}\lambda &= (220 + 1.36\rho)\\ &\quad \times 10^{-4}\ \mathrm{W/m\,K} \quad \left(\text{for } T_\mathrm{m} = 22.6^\circ\mathrm{C} \quad \text{and} \quad \rho = 120 - 350\,\mathrm{kg/m^3}\right)\end{aligned}$$

Concerning the compression-recovery of expanded (thermal) agglomerated cork when under a static load, studies indicate the following relations [2, 20, 21]:

$$d_\mathrm{a} = d_1 + 2d_2 \quad \text{and} \quad d_\mathrm{p} = d_1 + 3d_2$$

where d_a = maximum acceptable deformation; d_p = maximum foreseeable deformation; d_1 = deformation after 24 h; and d_2 = deformation in the period of 1–11 days.

Table 13.1 Average characteristics of expanded agglomerated cork (thermal)

Density	100–140 kg/m^3
Transfer coefficient (θm = 23 °C)	0.039–0.045 W/m °C
Specific heat (at 20 °C)	1.7–1.8 kJ/kg °C
Expansion coefficient (20 °C)	25–50 × 10^{-6}
Maximum pressure in elastic conditions	50 kPa
Elastic modulus (compression)	19–28 daN/cm^2 thermal
Diffusivity	0.18–0.20 × 10^{-6} m^2/s
Poisson's ratio	0–0.02
Water vapour permeability	0.002–0.006 g/m h mmHg
Modulus of rupture	1.4–2.0 daN/cm^2
Tensile strength, transversal	0.6–0.9 daN/cm^2
Tensile strength, longitudinal	0.5–0.8 daN/cm^2
Dimensional variation 23–32 °C, 50–90 % RH	0.3 %
Oxygen index	26 %
Tension deformation at 10 % (compression)	1.5–1.8 daN/cm^2
Temperature deformation (80 °C)	1.4–2.4 % (thickness)

Table 13.2 Average characteristics of expanded agglomerated cork (acoustic)

Density	<100 kg/m^3
Sound absorption coefficient (500–1,500 c/s)	0.33–0.8
Heat transfer coefficient (θm = 23 °C)	0.037–0.042 W/m °C
Modulus of rupture	1.4–1.6 daN/cm^2
Water vapour permeability	0.004–0.010 g/m h mmHg
Tensile strength, longitudinal	0.3 daN/cm^2
Water absorption (immersion)	9.2 %
(capillary action)	1.9 %
Dimensional variation 32–66 °C, 90–0 % RH	0.4 %

Regarding the acoustic absorption of expanded agglomerated cork, the thicker the material, the greater the noise absorption. With a reduction in thickness, maximum absorption moves to higher frequencies [20]. The type of noise to be blocked determines the most appropriate material to use.

Studies carried out regarding the transmission of low (L)-, medium (M)- and high (H)-impact noise on various sound insulation flooring types, including expanded agglomerated cork panels, obtained the following results [13]:

- Concrete slab at 250 kg/m^3
- Expanded agglomerated cork 25 mm, 108 kg/m^3: IL = 2 dB; IM = 19 dB; IH = 43 dB
- Expanded agglomerated cork 20 mm, 111 kg/m^3: IL = 0 dB; IM = 19 dB; IH = 47 dB
- Expanded agglomerated cork 25 mm, 132 kg/m^3: IL = 1 dB; IM = 16 dB; IH = 46 dB

- Expanded agglomerated cork 25 mm, 102 kg/m^3: IL = 2 dB; IM = 10 dB; IH = 40 dB
- Expanded agglomerated cork 40 mm, 120 kg/m^3: IL = 1 dB; IM = 24 dB; IH = 48 dB
- Expanded agglomerated cork 15 mm, 114 kg/m^3: IL = 1 dB; IM = 9 dB; IH = 41 dB
- Expanded agglomerated cork 10 mm, 112 kg/m^3: IL = 4 dB; IM = 9 dB; IH = 38 dB
- Expanded agglomerated cork 10 mm, 95 kg/m^3: IL = 4 dB; IM = 14 dB; IH = 43 dB
- Expanded agglomerated cork 20 mm, 191 kg/m^3: IL = 1 dB; IM = 21 dB; IH = 49 dB
- Expanded agglomerated cork 5 mm, 194 kg/m^3: IL = 1 dB; IM = 8 dB; IH = 39 dB
- Expanded agglomerated cork 25 mm, 260 kg/m^3: IL = 5 dB; IM = 21 dB; IH = 45 dB

The usage temperature limits in use for expanded agglomerated cork easily cover the scale of values found for use in buildings (from –20 to 90 ºC) without leading to degradation, deformation or irreversible alterations to cork's properties. Its composition allows it to withstand, without detriment, the application of molten bitumen, used to glue and waterproof terrace coverings [manufacturers' catalogues] and as can be seen in Fig. 13.10.

Fig. 13.10 Application of pure expanded agglomerated cork in roof insulation

Table 13.3 Thickness of expanded agglomerated cork according to the desired temperature inside the insulated system

Temperature (°C)	Thickness (cm)
–40 to –25	25–30
–25 to –18	20
–18 to –10	17.5
–10 to –4	15.0
–4 to +2	12.5
2–16	10.0
16–20	7.5
20	5.0

For uses in refrigerated chambers, the thicknesses usually considered are those stated in Table 13.3 and are dependent on the temperature to be maintained inside the chamber [18].

The properties required for a thermal-insulating material are low thermal conductivity coefficient, moisture absorbent, mechanical resistance appropriate for use, pliability, fire resistance, odour-free, not being prone to rodent attacks, durability, low density and price. Expanded agglomerated cork addresses these requisites quite well and is used, in particular, in low-temperature insulation areas [22] or for cargo-loading and/or visiting areas.

Expanded agglomerated cork is also one of the most advantageous insulating materials, since its density is comparatively high, and the same is true for its specific heat, leading to a very low thermal diffusion when compared to insulating materials with similar λ. It is, therefore, an excellent heat (or cold) preserver [23]. The thermal resistance provided by the standard thicknesses of expanded agglomerated cork easily guarantees the values stated in the directives regarding buildings' thermal characteristics [manufacturers' catalogues].

One of the important aspects to consider when applying thermal insulation, and more specifically expanded agglomerated cork, is determining the necessary insulation to attain specific thermal conditions and avoid surface condensation. According to [24], the elements on which the calculations are based are as follows:

The wall's transmission coefficient shall be given by

$$k = 1/\left(1/8 + e/\lambda' + 1/25\right)$$

The insulated wall's transmission coefficient shall be given by

$$k' = 1/\left(1/8 + e/\lambda' + e_1/\lambda + 1/25\right)$$

Thermal resistance R (=1/k) shall be given by

$$R = \left(1/8 + e/\lambda' + 1/25\right)$$

where k is the total wall transmission coefficient, which takes into account the transmission coefficient of each element; e the wall thickness; e_i the insulation thickness, to be determined; λ' the thermal conductivity coefficient of the wall elements; λ the heat transfer coefficient of the insulation; a_1 the interior film coefficient; a_2 the exterior film coefficient.

It is generally considered appropriate that: $k = 0.60$ kcal/m^2 h °C, $\lambda = 0.033$ kcal m/m^2 h °C, $a_1 = 8$, $a_2 = 25$–30.

For example, for a wall made up of two rows of cement blocks, 40 cm in thickness, with 2 cm of interior plaster and 2 cm of exterior plaster, by taking the table values for λ or k for building materials and elements, we get:

Blocks: $\lambda_1 = 1.0$; $e_1 = 0.40$; $k_1 = 1.0/0.40 = 2.5$; $R_1 = 1/2.5 = 0.400$.
Interior plaster: $\lambda_2 = 0.7$; $e_2 = 0.02$; $k_2 = 0.7/0.02 = 35$; $R_2 = 1/35 = 0.003$.
Exterior plaster: $\lambda_3 = 0.7$; $e_3 = 0.02$; $k_3 = 0.7/0.02 = 35$; $R_3 = 1/35 = 0.003$.

The wall's total resistance will be:

$$R_t = 1/8 + 0.400 + 0.003 + 0.003 + 1/25 = 0.571$$

Therefore, the total transmission coefficient will be:

$$k_t = 1/R_t = 1/0.571 = 1.75$$

The value of λ for expanded agglomerated cork is 0.033 kcal m/m^2 h °C, whereby the value of k for 1 cm of this material will thus be 3.3 and the respective resistance will be

$$R = 1/3.3 = 0.303$$

Considering the ideal value for the wall's transmission coefficient as being kcal/m^2 h °C, the resistance will be

$$R = 1/0.6 = 1.666$$

Since the walls had a value of $R = 0.571$, increasing this value to 1.666 with insulation would require

$$1.666 = 0.571 + 0.303 \cdot e_i \Rightarrow e_i = 3.6\,\text{cm}$$

Regarding surface condensation, however, the required insulation can be determined by applying the following empirical formula:

$$1/k = 0.15 \cdot (\Delta T - 22) + 3/(T/100 + 1) \cdot (95 - H)/5$$

where T is the interior ambient temperature; H the interior ambient humidity; ΔT the difference between the interior ambient temperature and the exterior minimum temperature.

The wall's coefficient, $1/k'$, should be subtracted from the coefficient $1/k$, obtained using the formula. Knowing that each centimetre of expanded agglomerated cork has a thermal resistance of 0.303, by dividing the result of the previous difference by this value, we find the number of centimetres of insulation necessary to avoid condensation.

Considering a typical case where $T = 20$ °C, $H = 80$ % and $\Delta T = 24$ °C, we would get:

$$R = 1/k = [0.15 \cdot (24 - 22) + 3]/[(20/100 + 1) \cdot (95 - 80)/5] = 0.916$$

Now considering the previous wall with $R_t = 0.571$,

$$e_1 = (0.916 - 0.571)/0.303 = 1.14\,\text{cm}$$

In this case, an insulator 1.14 cm thick would be sufficient to avoid condensation. As for thermal insulation, we would need 3.6 cm of expanded agglomerated cork, which would also avoid condensation.

Good thermal-insulating materials are usually good sound correctors and absorbers but poor sound insulators. There are three aspects to consider for the protection against noise [23]:

1. Insulation against sound through air transmission (e.g. from the street to the house interior)
2. Impact noise insulation (impacts on a floor or wall)
3. Sound absorption (reduction in reverberation or echo time)

As a wall filler, expanded agglomerated cork has a different vibration frequency to the exterior panels due to its elasticity and flexibility properties, which is an advantage. In terms of impact, expanded agglomerated cork may be used in a layer between the lining and the flooring itself (floating floors). As a ceiling and wall covering, it absorbs part of the total incident sound [23]. Some examples of its use can be seen in Fig. 13.11.

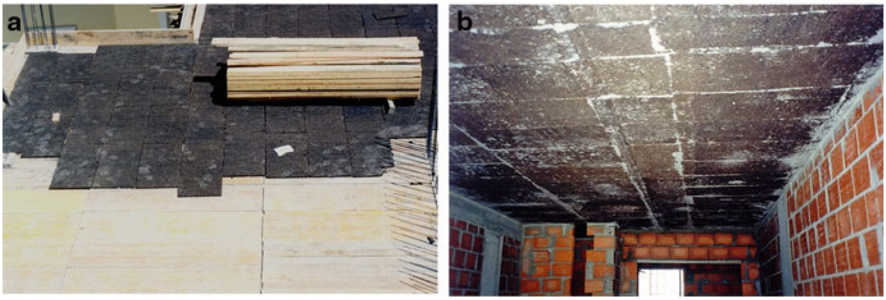

Fig. 13.11 Examples of applying insulation to slabs (thermal and sound)

The properties required for a sound-absorbing material are adequate absorption coefficient, durability, visual appearance, fire resistance, weight, light-reflection coefficient, method of application and cost. Expanded agglomerated cork is once again the material that best corresponds to most of these requirements. In the case of impact sound transmission, insulation can be achieved by using structural discontinuities, made possible with several types of agglomerated cork [22].

Expanded agglomerated cork is a sound absorber with a porous structure, which absorbs part of the incident sound energy. The absorption coefficient (α) of a material (at a given frequency) is the relationship between the sound energy absorbed by its surface and the incident energy. Expanded agglomerated cork has low absorption coefficients for frequencies lower than 800 Hz and higher absorption coefficients for higher frequencies up to 4,000 Hz. If its thickness is increased, it increases for frequencies lower than 800 Hz and decreases for higher frequencies [25].

It is also important to discuss the performance of expanded agglomerated cork in relation to humidity [23]. As is known, the insulating capacity of a material is reduced at the same rate that its moisture content increases, since the thermal conductivity of air is 0.023 kcal/m h °C (at 0 °C) and the thermal conductivity of water is 0.50 kcal/m h °C (at 0 °C). Water absorption depends on the chemical composition and alveolar or cellular characteristics of the material structure. Furthermore, besides moisture absorption and transmissibility, the fact that water is not stored inside the material is also important. Cork contains several hydrophobic elements which do not facilitate moisture retention.

As for its fire performance, tests carried out in accordance with the Federal American Standards (SS-A-118b) showed a noncombustible or fire-retardant result for expanded agglomerated cork at a nominal thickness of 50–76 mm [20, 26]. Flames produce surface carbonisation that gives rise to a practically noncombustible layer. The fumes released are considered to be non-toxic. They do not contain chlorides or cyanides, and the quantities of carbon monoxide and carbon dioxide released during combustion are around 0.6 % and 2.4 %, respectively [2], or between 0.1 % and 0.6 % and 0.1–2.3 % respectively, in accordance with the manufacturers' data. According to the ASTM-C-209 standards and the Schluter test, cork demonstrated good fire performance [23]. During one test, a block of expanded agglomerated cork, 2 in. thick, was placed on a Bunsen burner at a temperature of 1,500 °F, and it took 4 h for the flame to burn through. As a slow-burning material, cork forms a barrier against fire, and there have been cases where buildings have been saved from greater damage by this barrier [2, 21].

Expanded agglomerated cork in comparison to other organic insulation materials (e.g. cellular plastics) has advantages because it does not melt easily as they do. The other organic insulation materials end up totally losing resistance and form. Cork may be further protected by applying a coat of anti-fire paint. Furthermore, cork does not have compatibility problems with other contact materials and does not have any major problems interacting with solvents, resins, hydraulic binders, glues, bitumen, etc. [manufacturers' catalogues].

Here, mention should be made of an insulation product obtained by combining expanded agglomerated cork panels with coconut fibre panels, and there are also cases where it has been linked with synthetic materials.

In relation to the durability and useful lifespan of expanded agglomerated cork, when used, several cases can be mentioned (although some are not very recent, there are no major differences between then and now):

- In 1959, in Monza, a floor and a wall that had been insulated in 1922 were being rebuilt. The insulating material was in such perfect condition that it could be sold [27].
- The insulation installed on general refrigerators in Trieste immediately after the First World War was still in perfect condition after the Second World War [27].
- In 1996, a report was released that showed a study of the thermal conductivity of expanded agglomerated cork taken from the demolition of constructions aged 50 (refrigeration chamber) and 30 (building, laboratory). The results of the tests were the same as for new agglomerated cork, and its appearance was similar to cork insulation board that had just been made [28].

Agglomerated Cork for Vibration Insulation

For anti-vibration uses, the densest expanded agglomerated cork is used (e.g. 180–200 kg/m^3). It is applied mostly as a shock absorber in machinery support, as a way of reducing the transmission of vibration from the machine in operation to its structural base, with the same happening in foundation insulation [18] and, for example, underneath the rails.

Vibration insulation for machinery can also be performed by “rubber-cork” or “cork-rubber”, the name used depending on the amount of cork if it is less than or more than the amount of rubber (see the types in Fig. 13.12). It is also used as underlay for laminate flooring, for example.

In terms of performance as an anti-vibration insulator, a thicker-based expanded agglomerated cork makes for lower resonance frequency and greater resonance amplification. As far as density is concerned, the lower the value, the lower the resonance frequency but the greater the resonance amplification [29]. The natural frequency (f) of expanded agglomerated cork as an anti-vibration support is related to the final maximum deformation of the material (d) under a specific static load, via the formula $f = 5\sqrt{d}$, where f is in c/s and d in cm. Since F is the vibration frequency of the machine to be insulated (which is known), F/f must be greater than 4 [20, 23] for the vibrations to be effectively reduced. As the thickness of the agglomerated cork increases, its natural frequency decreases, improving insulation against vibration.

It should be noted that anti-vibration agglomerated cork provides good support for machines with rotation speeds of more than 1,200 rpm [30]. As examples of extreme maximum pressures recommend for anti-vibration agglomerated cork according to thickness, we have [manufacturers’ catalogues]:

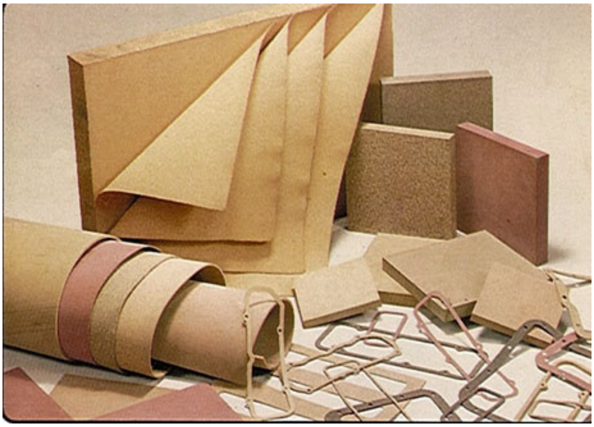

Fig. 13.12 Several types of "rubber-cork" products

Density 180 kg/m^3 and thickness 2.5 cm = 1.5 daN/cm^2
Density 250 kg/m^3 and thickness 10 cm = 2.5 daN/cm^2

In terms of lifespan, the following cases are usually cited [31]:

- Six rotary "super-palatia" machines were insulated against vibration using expanded agglomerated cork at Georges Lang Graphics in Paris, and the insulation was used continuously for more than 25 years.
- Other machines at "La Gazet van Antwerpen" were insulated with expanded agglomerated cork in 1927, and it was still being used in 1956.

Agglomerated Cork for Expansion Joints

Due to cork's high compressibility and recovery, certain types of composition cork are used in expansion joints. It is placed between the slab and the building's flooring and is also a good sound and thermal insulator.

Composition cork for expansion joints typically has characteristics including a 50 % reduction of the initial thickness for loads of 0.35–10.5 MPa, 90 % recovery of its original thickness after 50 % compression and expansion of nearly 6 mm for the same compression [1].

"Rubber-cork" can also be used for expansion joints.

Granulated and Regranulated Cork

Cork fragments with a particle size of more than 0.25 mm and less than 22.4 mm (see Fig. 13.13) are considered to be granulated. Particles smaller than 0.25 mm are considered to be cork powder [2, 21].

Fig. 13.13 Sample of granulated cork (original raw material)

Granulated and/or regranulated cork can be used as a final product as thermal insulation, to fill empty space in cavity walls or above the ceiling of the top floor of a building. Granulated cork is also used to prepare mortar with cement, to lessen the weight of certain building elements and even to manufacture construction parts or blocks.

Regranulated cork obtained from expanded agglomerated cork waste should also be mentioned. Its main use is to fill walls, terraces and roofs. It may also be used in concrete mixtures, as seen in Fig. 13.14.

The technical characteristics of regranulated cork (manufacturers' catalogues) are as follows:

- Density = 70–80 kg/m^3
- Heat transfer coefficient = 0.048 W/m °C
- Particle size = 0/3—0/15—0/10—3/15 mm

To insulate blocks of concrete against impact noise transmission, a layer of granulated cork can be used.

During an experiment [14] with a solid 250 kg/m^2 concrete slab, 4 cm thick, and laminate flooring over a 2 cm thick layer of granulated cork with a particle size of 0.5 mm and a density of 50 kg/m^3, the following reduction in impact noise transmission was observed:

Fig. 13.14 Example of the use of expanded regranulated cork

I Low—18 dB; I Medium—23 dB; I High—43 dB

The values for expanded granulated cork can be found in Table 13.4 [manufacturers' catalogues].

Standardisation for Cork Products for Construction

TC 16 is the technical standardisation committee, for cork, which was established in Portugal to deal with standards relating to cork. At international level, technical committee ISO/TC 87 was established. At European level, three European technical committees for standardisation cover areas directly related to some agglomerated cork uses: thermal expanded cork (CEN/TC 88), parquet (CEN/TC 134) and wall coverings using panels and rolls (CEN/TC 99) [32].

In Fig. 13.15, one of the current tests for cork coverings is shown (in this case abrasion).

Tables 13.5, 13.6, 13.7, 13.8, 13.9, 13.10, 13.11, 13.12, 13.13, 13.14, 13.15, 13.16, 13.17, 13.18, 13.19, 13.20, 13.21 show the standards for cork products for civil construction, with an indication of the requirements and test methods mentioned in the relevant standards (taken from [32] and updated according to [2]).

The ISO standards for cork have been revoked, except for those dealing with sound-absorbing agglomerated cork and joints, but they are still shown here as they are still used in some cases.

In recent years, architects, designers and decorators have become interested in natural materials again, including cork. The many different cork decoration

Table 13.4 Characteristics of lightweight concrete with regranulated cork

Mix	Volume		Weight/m^3	Compression resistance	Thermal conductivity
Cement	Sand	Regranulated cork	kg	daN/cm^2	W/m °C
1	0	6	400	2	0.13
1	0	4	500	6	0.18
1	2	6	900	11	0.24
2	3	8	1,100	17	0.60

Fig. 13.15 Abrasion test for cork flooring

Table 13.5 Granulated cork (characteristics, requirements and methods)

Characteristic	Requirement	Test method
Classification	By density and particle size	**NP 605** ISO 2031 and **NP 115** ISO 2030
Moisture content	$\leq$10 %	**NP 606** ISO 2190
Content in powder form	$\leq$0.4 %	**NP 115** ISO 2030

Sources—specification documents: NP 114:1994 and ISO 1997:1992

products that exist, with different textures, shades and colours, mean that different environments can be created for the most varied purposes, all with the comfort that is inherent to the material (see Fig. 13.16). Using cork in decoration has increased

Table 13.6 Composition cork (characteristics, requirements and methods)

Characteristic	Requirement	Test method
Thickness	Tolerance without nominal value:	
≤3 mm	±15 %	**NP 2372** ISO 7322
>3 mm	±15 %	
	0	
Density	To be declared by manufacturer	**NP 2372** ISO 7322
Compressibility recovery	To be declared by manufacturer	**NP 2372** ISO 7322
Tensile strength	≥200 kPa	**NP 2372** ISO 7322
Resistance to boiling water	Should not separate	**NP 2372** ISO 7322

Sources—specification documents: NP 114:1997 and ISO 1997:2000

Table 13.7 Composition cork for expansion joint filler (characteristics, requirements and methods)

Characteristic	Requirement	Test method
Length	Tolerance without nominal value:	**NP 1777**
	±6.4 mm	ISO 3867
Width	Tolerance without nominal value:	**NP 1777**
	±3.2 mm	ISO 3867
Thickness	Tolerance without nominal value:	**NP 1777**
	±0.15 mm	ISO 3867
Density	To be declared by manufacturer	**NP 1777**
		ISO 3867
Recovery	≥140 % of initial thickness	**NP 1777**
		ISO 3867
Compression	≥340 and ≤1035 kPa	**NP 1777**
		ISO 3867
Extrusion	≤6.4 mm	**NP 1777**
		ISO 3867
Recovery	≥140 % of initial thickness	**NP 1777**
		ISO 3867
Compression	≥340 and ≤1035 kPa	**NP 1777**
		ISO 3867
Extrusion	≤6.4 mm	**NP 1777**
		ISO 3867
Expansion in water	≥140 % of initial thickness	**NP 1777**
(Only applies to self-expanding agglomerated cork)		ISO 3867

Sources—specification documents: NP 1778:1997 and ISO 3869:2001

Table 13.8 Sound-absorbing composition cork (characteristics, requirements and methods)

Characteristic	Requirement	Test method
Side length	Nominal value: 300 mm	**NP 2804**
	Tolerance: ±1 mm	ISO 9366
Thickness	Minimum value: 4.8 mm	
	Tolerance:	**NP 2804**
w/o bevel	±0.2 mm	ISO 9366
w/bevel	±0.3 mm	
Straightness of sides	≤0.3°	**NP 2804**
Rectangularity	≤1.5 mm	ISO 9366
Tensile strength	≥200 kPa	**NP 2372**
		ISO 7322
Noise absorption (reverberation chamber)	Graph showing absorption for each frequency band tested	
		NP EN 670
		ISO 354

Sources—specification documents: NP 1552:1997 and ISO 2510:2001

Table 13.9 Sound-absorbing pure cork (characteristics, requirements and methods)

Characteristic	Requirement	Test method
Length	Tolerance: ±0.4 %	**NP 1551**
	Maximum 3 mm	ISO 2509
Thickness	Minimum: 20 mm	**NP 1551**
	Tolerance: ±0.4 mm	ISO 2509
Straightness of sides	≤0.3°	**NP 2804**
		ISO 9366
Modulus of rupture (for thicknesses ≥ 20 mm)	≥140 kPa	**NP 603**
		ISO 2077
Moisture content	≤4 %	**NP 1042**
		ISO 2066
Noise absorption (reverberation chamber)	Graph or table showing absorption for each frequency band	**NP EN 670**
		ISO 354

Sources—specification documents: NP 1552:1997 and ISO 2510:2001

its popularity among professionals and in the do-it-yourself market. Particularly in the latter, modern application systems (using glue, rolls, locking, etc.) have made it easier to install [1, 2].

Table 13.10 Expanded agglomerated cork (characteristics, requirements and methods)

Characteristic	Requirement	Test method
Thermal conductivity	$\leq$0.060 W/m K	ISO 8302
Thermal resistance	$\geq$ 0.025 m^2 K/W	ISO 8301
Length	Class L1:	NP EN 822
	Nominal value ±3 mm	
	Class L2:	
Tolerance	Nominal value ±5 mm	
Width	Class W1:	NP EN 822
	Nominal value ± 2 mm	
	Class W2:	
Tolerance	Nominal value ± 3 mm	
Thickness	Tolerance:	NP EN 823
25 mm < thi[a] $\leq$ 50 mm	Class T1: ±1 mm	
thi[a] > 50 mm	Class T2: ±2 %	
	w/maximum 2 mm	
Straightness of sides		
Length and width	$\leq$4 mm/m	NP EN 824
Thickness	$\leq$2 mm/m	
Flatness	$\leq$2 mm	NP EN 825
Dimensional stability at (23 ± 2)°C and (50 ± 5)% RH length and width	$\leq$0.5 %	NP EN 1603
Flatness	$\leq$1 mm/m	
Dimensional stability under specified temp. and humidity length and width	$\leq$0.5 %	NP EN 1604
Flatness	$\leq$1 %	
Deformation under specified compressive load and temperature conditions	$\geq$DLT	NP EN 1605
Bending strength	$\geq$130 kPa	EN 12089 Method B
Moisture content	$\leq$8 % (m/m)	NP EN 12105
Fire resistance	Classification	NP EN 13501-1
Apparent density	$\leq$130 kg/m^3	NP EN 1602
Compression behaviour (10 % deformation)	CS Level (10) 90 $\geq$ 90 kPa CS	NP EN 826
	Level (10) 100 $\geq$ 100 kPa CS	
	Level (10) 110 $\geq$ 110 kPa	
Point load	$\geq$Declared level	NP EN 12430

(continued)

Table 13.10 (continued)

Characteristic	Requirement	Test method
Compressibility		NP EN 12431
Thickness	$\leq$Declared value	
Compressibility	$\leq$Declared value see	
Long term reduction	Below	
Compressive creep	See below	EN 1606
Tensile strength perpendicular to faces	TS level $40 \geq 40$ kPa	NP EN 1607
	TS level $50 \geq 50$ kPa	
	TS level $60 \geq 60$ kPa	
Bending behaviour	$\geq$130 kPa	EN 12089 Method B
Shear behaviour	$\geq$50 kPa	NP EN 12090
Water absorption (short term)	$\leq 0.5\ \text{kg/m}^2$	NP EN 1609 Method A
Water vapour transmission	$\geq$Declared value	NP EN 12086
Apparent density	$\geq$Declared value	EN 1602
Air flow resistance	$\geq$Declared level	EN 29053
Acoustics	$\geq$Declared value	EN ISO 354:1993/A1
		EN ISO 11654

Source—specification document: NP EN 13170: 2001

In terms of insulation (see Fig. 13.17), the possibilities for using expanded agglomerated cork in civil construction are [1]: Terraces—thermal insulation, vibration insulation, moisture condensation insulation and waterproofing; walls and roofs—thermal insulation, condensation prevention; partitions and doors—thermal and sound insulation; walls and ceilings—sound correction, thermal insulation, comfort, decoration; floors—vibration and thermal insulation; bridges—thermal insulation, expansion/contraction joints.

More specifically, we have thermal insulation for buildings (ceiling, floors and walls)—insulation for the exterior walls (façades), insulation for cavity walls (air space), insulation for flat roofs, thermal insulation for roofs and attics, thermal insulation for ground floors and thermal insulation for refrigeration rooms—against varying temperature, reducing loss of energy, protecting slabs and, furthermore, stopping or reducing surface condensation on walls and ceilings. One of the main uses of expanded agglomerated cork is thermal insulation on the outside of roofs, where it helps waterproofing and where its resistance to high temperatures and mechanical characteristics is advantageous. For exterior insulation, agglomerated cork panels are glued to the outer surface of the wall, and an appropriate finish is applied later ([2, 21], manufacturers' catalogues), for example, plaster (see Fig. 13.18).

Table 13.11 Pure expanded agglomerated cork in panels for thermal insulation (characteristics, requirements and methods)

Characteristic	Requirement	Test method
Length		NP EN 426
Rolls or sheets:	≥Nominal value	
Width	Tolerance without nominal value: ≤0.15 %	NP EN 426
Thickness of backing layer	≥Nominal value	NP EN 429
Straightness of sides		
Rectangularity		
≤610 mm:	≤0.35 mm	NP EN 426
≤610 mm:	≤0.50 mm	
Residual indentation		NP EN 433
Average value	≤0.25 mm	
Dimensional stability		NP EN 434
Variation permitted:	≤0.4 %	
Tear resistance		ISO 434
Average value:	≥20 n/mm	(Method B, Test A)
Flexibility	Cracks should not appear	NP EN 435 (20 mm mandrel)
Abrasion resistance	≥250 mm^3	ISO 4649 Method A
		(Vertical load (5 ± 0.1) N)
Hardness	≥75 Shore A	ISO 7619
Peel resistance	Average value ≥ 50 n	NP EN 431
Colour fastness to art. light	Minimum 6	ISO 105-BO2 Method 3
Resistance to cigarettes		NP EN 1399
Stubbed:	≤1	
Burning:	≤4	

Source—specification document: NP EN 1817:1999

Another specific use of thermal insulation, where the densest expanded agglomerated cork is used, is in refrigeration facilities in areas where fixed or mobile pressure is exerted [1, 18]—specifically on the floor of the chambers, where goods are placed, people pass through and loading/unloading equipment is used.

In terms of noise, we have sound correction through noise absorption and a reduction in reverberation time (reducing echo) in certain settings, also by reducing impact noise in special uses. These uses include agglomerated cork parquet, laminate flooring and in cases where cork products are used as discontinuity between rigid elements.

Anti-vibration insulation, for which the densest expanded agglomerated cork is also used, is applied mostly as a shock absorber for the machinery support, as a way of reducing the transmission of vibration from the machine in operation to its

Table 13.12 Agglomerated cork floor tiles (characteristics, requirements and methods)

Characteristic	Requirement	Test method
Side length	Deviation from nominal value	ISO 9366
	≤ 0.2 % and maximum 1 mm	NP EN 427
Total thickness (individual results)	Deviation from nominal value	ISO 9366
With finish:	0–0.25 mm	NP EN 428
Without finish:	0–0.50 mm	ISO 9366
Straightness of sides and rectangularity		
Side $\leq$ 400 mm:	≤ 0.50 mm	NP EN 427
Side $>$ 400 mm:	≤ 1 mm	
Apparent density		NP EN 433
Average value:	$\geq$Nominal	
Individual values:	≥ 95 % Nominal	
Mass per unit area		NP EN 430
Average value:	Nominal $\pm$ 10 %	
Dimensional stability		
Variation permitted:	≤ 0.4 %	NP EN 434
Curling	≤ 6 mm	NP EN 434
Moisture content	To be declared by manufacturer	NP EN 12105

Source—specification document: NP EN 12104: 2000

structural base, with the same happening in foundation insulation. Agglomerated cork is especially recommended for use in anti-vibration mats, especially for high frequencies [10]. They are also used as contraction/expansion joints between rigid elements.

The types of floor coverings based on cork are varied and may be categorised as [2, 21] cork tiles, agglomerated cork tiles with elastomer, agglomerated cork tiles with PVC, vinyl coverings over resilient supports made of cork and agglomerated cork with PVC backing, rubber-cork coverings, and laminate flooring with cork as an upper and/or lower layer.

There are also some specific uses for granulated cork in civil construction [2, 21]:

1. Lightweight filler to improve insulation
2. Inert material in concrete manufacturing to reduce the weight of concrete panels
3. Thermal insulation in concrete and screed
4. Anti-condensation for walls and coverings
5. Noise insulation for laminate flooring
6. Filler for cavity walls

Table 13.13 Agglomerated cork floor tiles with a usage layer made of (poly)vinyl chloride (characteristics, requirements, methods)

Characteristic	Requirement	Requirement test method
Side length	Deviation from nominal value	NP EN 427
	≤0.1 % and maximum 0.5 mm	
Thickness (usage layer)	Tolerance without nominal value:	NP EN 429
Average value:	+0.18 mm	
	–0.15 mm	
Individual values:	±0.20 mm	
Straightness of sides and rectangularity		NP EN 427
Side ≤ 400 mm:	≤0.25 mm	
Side > 400 mm:	≤0.35 mm	
Dimensional stability	≤0.4 mm	NP EN 434
Curling	≤6 mm	NP EN 434
Mass per unit area	Tolerance without nominal value:	NP EN 430
Average value:	+13 %	
	–10 %	
Density (usage layer)	Tolerance without nominal value:	NP EN 436
Average value:	±0.05 g/m^3	
Thickness of backing layer	Tolerance without nominal value:	NP EN 429
Average value:	±10 %	
Peel resistance		NP EN 431
Average:	≥35 n/50 mm	
Individual values:	≥125 n/50 mm	

Source—specification document: NP EN 655:1997

Usage Methods

One of the aspects to take into account when using cork products, particularly parquet flooring, to avoid problems that are not actually caused by the product, involves preparing the base, gluing and conserving/upkeeping.

The subfloor should therefore be cleaned and made even, and a quick-drying contact adhesive should be used. The surface should be properly prepared before application (hygroscopic balance). A period of 48 h is normally recommended. It is also important to ensure that the surface to be covered has hygroscopic balance when the flooring is applied. If the surface is screed, its residual moisture must not be greater than 2.5 %. If the surface alkalinity is greater than 10, it should be neutralised before application [manufacturers' catalogues].

In refurbishment works, all of the former floorings should be removed and the subfloor should be completely levelled out and cleaned. If glue is used (e.g. with tiles), it should be compatible with cork (acrylic, neoprene).

After it has been laid, the flooring should be maintained in accordance with the type of finish and in accordance with the level of traffic.

The best way to reduce impact noise transmission through the floor consists of leaving a discontinuity between the flooring and the load-bearing subfloor. Several

Table 13.14 Floor covering panels for use in floating floor systems (characteristics, requirements and methods)

Characteristic	Requirement	Test method
Dimensions measured on the usage panel	Deviation from nominal value	NP EN 427
Square panels		
Length and width	±0.10 % w/max 0.5 mm	
Rectangular panels		
Width	±0.10 % w/max 0.5 mm	
Length	max 2.0 mm	
Total thickness		NP EN 428
Average	Nominal ± 0.25 mm	
Individual values	Maximum deviation from average:	
	±0.30 mm	
Straightness of sides		NP EN 427
Rectangularity	≤0.50 mm	
Measured on the usage layer	≤0.30 mm	
Panel flatness in relation to length		
Width		
Concave/convex	≤0.50 %/≤1.0 %	NP EN 14085
Concave/convex	≤0.10 %/≤0.15 %	Annex A
Gap between panels		
Average	≤0.15 mm	NP EN 14085
Individual values	≤0.20 mm	Annex B
Unevenness between panels		
Average	≤0.15 mm	NP EN 14085
Individual values	≤0.20 mm	Annex B
Dimensional variation caused by alterations in air humidity	≤5 mm	NP EN 14085
		Annex C

Source—specification document: NP EN 14085:2003

types of cork products may be used for this, including expanded agglomerated cork and composition cork.

For laminate flooring, the MDF or HDF intermediate layer has a tongue-and-groove interlocking system or click-lock system. The former system is glued together (usually using a line of PVA glue applied to the tongue edge), and in the latter pressure is applied until the boards lock together (sometimes this is done using a block) [2].

There are some recommendations for installing/maintaining laminate floor systems [manufacturers' catalogues], which are as follows:

Table 13.15 Agglomerated cork underlay for floor coverings (characteristics, requirements and methods)

Characteristic	Requirement	Test method
Length and width		NP EN 426
Rolls or sheets	≥Nominal value	
Total thickness	Tolerance without nominal value:	NP EN 428
≤5 mm	±0.2 mm	
>5 mm	±5 %, maximum 0.5 mm	
Mass per unit area	Tolerance: nominal value ± 10 %	NP EN 430
Tensile strength	≥200 kPa	ISO 7322
Flexibility	Should not snap or crack	NP EN 435, Method A
Moisture content	To be declared by manufacturer	NP EN 12105
Reduction of impact sound	To be declared by manufacturer	ISO 140-6 or ISO 140-8

Source—specification document: NP EN 12103:1999

Table 13.16 Agglomerated cork panels for wall coverings (characteristics, requirements and methods)

Characteristic	Requirement		Test method
Side length	Tolerance without nominal value: ±0.5 %		NP EN 427
Total thickness	Minimum:	Tolerance:	NP EN 428
Type I:	10 mm	±0.8 mm	
Types II and III:	2 mm	±0.3 mm	
Straight sides and rectangularity			NP EN 427
Side ≤ 400 mm:	≤0.5 mm		
Side > 400 mm:	≤1 mm		
Tensile strength	≥300 kPa		ISO 7322
Dimensional stability	Maximum variation: ≤0.4 %		NP EN 434
Curling	≤6 mm		NP EN 434
Moisture content	≤7 %		
Apparent density	To be declared by manufacturer		NP EN 672
Joint resistance	Should not peel		ISO 8724
Formaldehyde content	≤95 mg/kg		NP EN 12149

Source—specification document: NP EN 12781:2001

- Avoid using this type of flooring in very humid locations (bathrooms, laundry rooms, saunas).
- Put a polyethylene film in place before laying the flooring.
- Leave an 8–10 mm gap between panels and walls (dimensional variation).
- Do not attach the flooring directly to the subfloor (glue, nails, screws).
- Clean with a vacuum cleaner or with a slightly damp cloth, and do not directly apply water.

Table 13.17 Agglomerated cork rolls for wall coverings (characteristics, requirements and methods)

Characteristic	Requirement	Test method
Dimensions		NP EN 426
Width:	Tolerance without nominal value: ±1 %	
Length:	≥Nominal value	
Total thickness	Tolerance without nominal value: ±0.3 mm	ISO 7322
Rectangularity	Tolerance: 1 % for every 5 m of length	NP EN 427
Tensile strength	≥200 kPa	ISO 7322
Moisture content	≤7 %	
Flexibility	Cracks should not appear	ISO 4708
Formaldehyde content	≤95 mg/kg	NP EN 12149

Source—specification document: NP EN 13085:2001

Table 13.18 Agglomerated cork with rubber for floor coverings (classification)

Classification requirements							
Class/usage level	**21**	**22**	**23**	**31**	**32**	**33**	**34**
Total thickness	3.5 mm						
Usage layer thickness	1.0 mm						
Chair with wheels	Surface appearance should not significantly change						

Source—specification document: NP EN 1817:1999

Table 13.19 Agglomerated cork floor tiles with a usage layer made of (poly)vinyl chloride (classification)

Classification requirements									
Class/usage level	**21**	**22**	**23**	**31**	**32**	**41**	**33**	**42**	**34**
Total thickness	2.0 mm		2.5 mm		3.5 mm		0.50 mm		0.65 mm
Usage layer thickness	0.15 mm	0.20 mm	0.25 mm		0.35 m		0.50 mm		0.65 mm
Residual indentation	Average: ≤0.30 mm				Average: ≤0.20 mm				
Joint resistance	Average: ≥150 n/50 mm								
	Individual values: ≥120 n/50 mm								
Chair with wheels	–				No significant alterations should occur				
Furniture leg:	–	No significant alterations should occur on the surface (leg 3)			No significant alterations should occur on the surface (leg 2)				
Furniture leg on soldered joints	–				No significant alterations should occur on the surface (leg 0)				

Source—specification document: NP EN 655:1997

Table 13.20 Agglomerated cork floor tiles (classification)

Classification requirements						
Class/usage level	**21**	**22**	**23**	**31**	**32**	**41**
Total thickness	$\geq$3.2 mm		$\geq$4 mm			
Apparent density	$\geq$400 kg/m^3	$\geq$450 g/m^3 (w/ or w/o decoration)			$\geq$500 kg/m^3 (w/ or w/o decoration)	
Residual indentation	$\leq$0.4 mm				$\leq$0.3 mm	
Chair with wheels					No significant alterations should occur	
Furniture leg					No significant alterations should occur (leg 2)	

Source—specification documents: NP EN 12104:2000

Table 13.21 Floor covering panels for floating floor systems—cork usage layer (classification)

Classification requirements					
Class/usage level	**21**	**22**	**23**	**31**	**32**
Nominal thickness for the cork usage layer	$\geq$2.5 mm			3.0 mm	

Source—specification document: NP EN 14085:2003

To avoid undesirable condensation inside the building features that use expanded agglomerated cork (and other similar products) as thermal insulation, vapour barriers like polyethylene film are applied to the interior side of the products [manufacturers' catalogues].

For façade insulation, expanded agglomerated cork should be glued using an adhesive putty, and, with staggered joints, smoothing mortar is applied, followed by a fibreglass frame and then plaster. To insulate flat roofs, a vapour barrier is installed after smoothing, followed by the cork panels in a staggered pattern. A bituminous layer is applied, followed by a protective filter and last of all gravel [manufacturers' catalogues].

When preparing a lightweight concrete with regranulated expanded cork, the regranulated cork should first be mixed with a little water to moisten it, and then cement and possibly sand should be added (manufacturers' catalogues).

Maintenance and Cleaning

Agglomerated cork flooring is durable, especially if it is looked after and maintained properly. It should not be used in areas that are constantly in direct sunlight as this has a tendency to cause discolouration. The flooring's durability and resistance and the type of maintenance and use are directly linked to the type of finish applied: wax, varnish or PVC coating. Cork flooring is recommended for places for everyday use, and normally fixed or movable furniture is not a problem. Cork is also appropriate for places where everyday cleaning is normally done using water, as cork can cope with contact with water provided it is not systematic or over

Fig. 13.16 Examples of the use of cork wall and floor coverings

Fig. 13.17 Example of the use of expanded agglomerated cork in roofing

Fig. 13.18 Example of the use of expanded agglomerated cork in façades

a long time. Cork flooring is practically stain-resistant against products normally used at home. It is recommended that cork flooring is cleaned using a vacuum cleaner or a slightly damp mop [2].

When the varnish needs to be reapplied, all products used should be removed, the floor then sanded carefully, dust removed and 1 or 2 coats of the recommended varnish applied. Furniture should not be dragged over the surface of the floor, and furniture legs should be protected [manufacturers' catalogues].

As for wall coverings, the steps taken are similar to those for flooring [2]. Exposed insulation is normally painted using water-based paint, and each coat may be renewed simply by painting over the previous coat [2]. There are no special maintenance or cleaning steps to be considered for other cork products for civil construction [2].

13.4 Cork Products in the Context of Construction Products Directive

After the technical harmonisation necessary to meet the requirements of the Construction Products Directive, two main areas of construction products were defined to create the harmonised standards, thermal-insulating materials and flooring products, which include cork products (CEN/TC-88, expanded agglomerated cork was included in the first, and CEN/TC-134, cork flooring included in the second). In 1992, following the reactivation of the technical committee for wall coverings, a working group for the cork area (CEN/TC 99/WG 3) was also formed [32].

The directive on construction products 89/106/EEC was published in December 1989 but was partially amended by Directive 93/68/EEC and clarified by the Commission Decision of 31 May 1995 and by later documents relating to processes for proving conformity applied to certain ranges of products (which included cork products, e.g. thermal insulation materials) [2].

The directive (often known as CPD) established the platform necessary to eliminate the technical barriers on determining which products should comply with the so-called essential requirements relating primarily to health and safety criteria. These requirements are reference criteria to be met by the products. But for the industry to meet these requirements without creating unfair competition, the functional performance and technical specifications of the construction products should be set in European standards—the so-called harmonised standards—applicable in all states. The CPD also determines the basic steps that should be taken to check the products' conformity to these requirements [32].

A harmonised standard is a technical specification (European standard or harmonised document) adopted by the CEN—European Committee for Standardization. Implementation of the CPD is therefore aided by establishing harmonised European standards (hEN) that perform a practical and important role in its application. hEN are voluntary, like other European standards, but are developed around essential requirements and based on commission mandates (Directive 98/34/EC). Their references are published in the official journal and transposition into national standards is compulsory. After they are transposed, the national standards applying to the same field are revoked [2].

The directive further considers that a product is suitable for use if it complies with a harmonised standard. Compliance is shown using a CE marking, and using the marking is entirely the manufacturer's responsibility.

13.5 Ecological Aspects Related to Cork Products

Reuse and Recycling

After use, often due to the end of the building's usable life, the expanded agglomerated cork panels are entirely recovered whenever possible. They can be used again in similar situations, since recovery from buildings over 50 years old has shown that even after that many years the aspects and properties of expanded agglomerated cork panels remain unchanged [28, 33].

If it is not possible to recover the cork products (due to broken panels or contamination by other products), it can be crushed to obtain regranulated cork that is used just like clean granulated cork in thermal insulation or as inert material in concrete and lightweight mortar manufacturing [33].

Granulated cork, when it is not mixed, can also be reused as a filler or in the manufacture of agglomerated cork or in mortars. If the process of obtaining cork products does not use contaminants (film, glue, mortar, etc.), the cork can be ground and used or integrated into technical products.

Composition cork for civil construction can include several types of waste made of other cork products (e.g. used cork stoppers, leftover agglomerated cork, etc.), helping boost the overall recycling capacity.

Ecological Aspects

Manufacturing expanded agglomerated cork requires only superheated steam, using boilers fuelled by the waste from grinding and finishes. No other products other than cork are introduced, and considering that agglomeration is based on resins from the cork itself, this is a 100 % natural and environment-friendly product, an advantage that is very difficult to find among other products with similar uses [2].

The transformation process for cork construction products produces an important waste product, cork powder. The powder is currently burnt to produce the steam and/or energy used in factories, thanks to the high energy content that the material has. All industrial cork waste is reused or reclaimed/recycled in another way [2].

The fact that cork products are used is also very important from an ecological standpoint, because cork is a renewable product, used in long-life products, helping boost CO_2 sequestration. Furthermore, a cork oak tree that is periodically stripped will produce between 250 and 400 % more cork [1] than it would if it were not been stripped, thereby increasing CO_2 sequestration. For that reason, using cork products, which means harvesting the material, encourages the formation of more cork and therefore more CO_2 sequestration [34]. These types of products also are very long-lasting and retain the carbon that forms them during their lifespan. They are “carbon-neutral” when decomposing or used to generate energy.

If we consider the average value of 94,700 tonnes of cork construction products that make up Portuguese exports (in 2007; see point 13.1.4) and knowing that cork’s average carbon content is 57.37 % [34], it means 54,330 tonnes of carbon per year are held in cork, which is equivalent to 199,065 tonnes of CO_2 sequestered/year (CO_2: $C = 3.664$ (w/w)). Considering that the average distance driven by a motor vehicle is 17,500 km per year and that average emissions are 170 g CO_2/km, in one year that vehicle will produce 2.98 tonnes of CO_2. We can conclude therefore that the 54,330 tonnes are equivalent to the pollution produced by around 66,800 cars/year.

13.6 Future Cork Products for the Civil Construction Industry

A new cork-based product is being introduced in the market, consisting of a flexible tubular covering made using extrusion. It is designed for use in industrial and residential settings, for mechanical, thermal and sound insulation, specifically for exterior conditions in which wear produced by photochemical, chemical, physical and biological action is high. It has better resistance (greater durability, fire resistance, UV ray performance and temperature variation) than comparable materials (e.g. polyurethane foams, materials derived from polyester). Wide usage is foreseen (see example in Fig. 13.19) as insulation for air conditioning piping, solar water heating systems, etc. The material can also be buried in the ground or used in construction and has a thermal conductivity of around $0.05\ \mathrm{W\ m/m^2\ h\,°C}$.

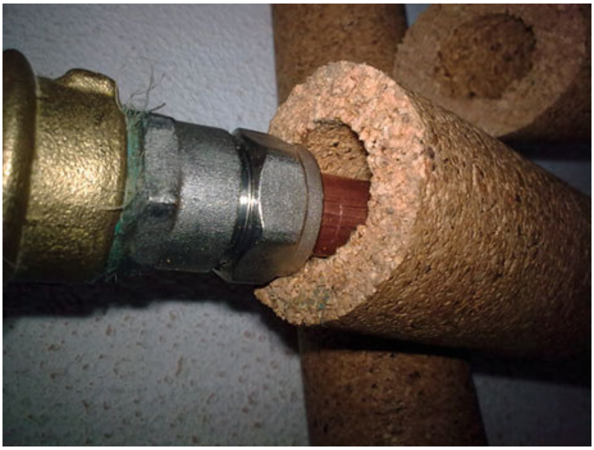

Fig. 13.19 Tubing insulation with extruded agglomerated cork

Future evolution of expanded agglomerated cork will include using densification techniques that have already been developed, providing different physical and mechanical characteristics but keeping the special environmental properties, thereby increasing the number of possible uses and expanding the market [35, 36].

Agglomerated cork for coverings and decorations also has a future, since there has been a growing trend in the use of natural products for these purposes. Diversifying patterns and combinations with other materials will also be important, and market studies and advertising aimed at opinion makers, such as decorators, designers, architects and civil engineers, shall be particularly relevant.

In the composition cork area, the industrial production of rigid agglomerated cork with plastic-binding agents [37] has yet to be explored, but it would broaden the uses and allow industrial waste to be reused with greater added value.

It is thought that in the future there will be an increase in the use of cork products in conjunction with other materials, of which there is an example in Fig. 13.20 [38], for structural purposes, as well as other very high value-added uses, such as innovative applications in the construction sector and other specific fields.

In this sector, some other products that have already been studied but are not yet in the market are also worth noting, including agglomerated cork with binding agents based on lignin waste, products made with mortar, plaster, cork mixtures, etc.

A summary of possible products incorporating cork for future use in civil construction can be found in [39].

The structural use of some construction features made with cork is also predicted, as well as the use of three-dimensional parts (uneven, relief formats), helping to provide greater architectural value.

Finally, a new product for cleaning/removing dirt from materials exposed to environmental pollution has been studied, based on projecting organic particles obtained from cork industry waste. Many new applications are envisaged, to clean

Fig. 13.20 New products based on cork and carton-packaging waste

monuments and building façades, and this may be another important use of cork products in civil construction.

References

1. Gil L (1998) Cortiça—Produção, Tecnologia e Aplicação. Ed INETI, Lisbon
2. Gil L (2007) Manual Técnico: Cortiça como Material de Construção. Ed. APCOR, Stª Mª Lamas
3. Oliveira MA, Oliveira L (2000) The Cork. Ed. Corticeira Amorim, Rio de Mouro
4. Fernandez LV (1971) Aglomerados Negros de Corcho—Partes I e II. AITIM, Série C, n.° 44, Madrid
5. APCOR-Anuário (2009) Anuário APCOR. Ed. APCOR, Santa Maria Lamas
6. EGF (1982) Análise Tecnológica do Sector Corticeiro, vols I e II. Lisbon
7. Pereira JCS (1988) Suplemento Boletim IPF-Cortiça. n.° 600, p 211–218
8. Silva HL (1982) Bol. IPF—Cortiça, n.º 520, p 31–32
9. Gil L (1987) Cortiça—Tecnologia de Processamento e Constituição Química, monografia do curso de mestrado em Química Orgânica Tecnológica, UNL/LNETI, Ed. DTIQ, n.° 3, Lisbon
10. Garret A (1946) Cortiça Aplicada. Ed. Altura, Porto
11. Gibson LJ, Ashby MF (1988) Cellular solids structure and properties. Pergamon Press, Oxford
12. Anónimo (2005) Notícias APCOR, n.° 41, p 13
13. Anónimo (1973) A Cortiça no Isolamento Sonoro de Pavimentos, separata Bol. JNC, Lisbon
14. LEEC (1977) Bol. IPF—Cortiça, n.°s 469 e 470, p 567–568 e 595–596
15. LEEC (1978) Bol. IPF—Cortiça, n.° 472, p 49–50
16. Borges M (1986) Bol. IPF—Cortiça, n.° 573, p 205–207
17. Fernandez LV (1984) Estanquidad, Dezembro, p 29–34
18. Medeiros H (n.d.) ABC Insulation Corkboard. Ed. JNC, Porto
19. LEEC (1974) separata Bol. IPF—Cortiça, n.° 427

20. Fernndez LV (1974) Estudio de la calidad de los aglomerados de corcho acusticos y vibraticos AITIM, série C, n.° 62, Madrid
21. Gil L (2005) Cortiça, in Materiais de Construção: Guia de Utilização. Ed. Loja da Imagem, Lisboa, p 96–127
22. Andrade A (1962) Thermic and acoustic insulation, separata Bol JNC. Lisbon
23. Fernandez LV (1987) Bol. IPF—Cortiça, n.° 587, p 222–229
24. Lissia F (1977) Bol. IPF—Cortiça, n.° 469, p 553–561
25. Anónimo (1986) Bol. IPF—Cortiça, n.° 569, p 65–67
26. Pinto R, Melo B (1988) Bol. IPF—Cortiça, n.° 602, p 322–338
27. Lissia F, Pes A (1967) Bol. JNC, n.° 339, p 4–8
28. Gil L (1996) In: International conference application of life cycle assessment in agriculture. Food and Non-Food Agro-Industry and Forestry, Brussels
29. Prates MJL (1993) Características e Comportamento Mecânico de Aglomerados. Negros de Cortiça. Dissertação do curso de Mestrado em Engenharia Mecânica, IST, Lisbon
30. Andrade A (1948) Bol. JNC, n.° 122, p 61–66
31. Katel IE (1956) Bol. JNC, n.° 207, p 67–73
32. Bicho MF, Gil L (1999) Cortiça—Guia Normativo. Ed. IPQ/CTCOR, Lisbon
33. Gil L (2002) In: World renewable energy congress VII, Cologne, p 705
34. Gil L (2005) Rev. Indústria & Ambiente, n.° 38, p 10–11
35. Gil L (1999) Patente Portuguesa n.° 100647
36. Gil L (2001) Cortiça Revista, n.° 1, p 41–42
37. Gil L (1999) Patente Portuguesa, n.° 101915
38. Gil L (2003) Patente Portuguesa, n.° 102992
39. Gil L (2009) Materials 2(3):776–789

Nanomaterials

14

M. Clara Gonçalves

Abstract

Over the past 10 years the word *nano* has become mainstream. *Nano* is being seen and heard in films, on the radio, on television, and in press. *Nano*material, *nano*scale, *nano*science, *nano*technology, and *nano*fabrication are the key words of this new paradigm. But how can nanotechnology be defined? Nanotechnology is all about the study and development of new functional artificial materials/systems whose structures and components exhibited novel and significantly improved physical, chemical, and biological properties, due to their *nano*scale size.

The civil engineering productive sector is traditionally conservative and fragmented, being mainly comprised by small- and medium-sized companies. This is one of the main factors why investigation and development of nanoproducts in civil engineering is still in its beginnings, when compared with pharmaceutical and medicinal sectors. Nevertheless, there are some new (or traditional improved) civil engineering nano-based materials onto the market, many still in development or testing—some case studies are presented here.

Keywords

Nanomaterial • Nanoscale • Wulff diagram • Magic numbers • Homogeneous nucleation • Heterogeneous nucleation • Lattice mismatch • Gibbs-Thomson effect • Ostwald ripening • Enhanced-traditional materials • Eco-active materials • Self-healing materials • Antibacterial materials • Photo-voltaic materials • Nanotoxicology

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M.C. Gonçalves, F. Margarido (eds.), *Materials for Construction and Civil Engineering*, DOI 10.1007/978-3-319-08236-3_14

14.1 Introduction to Nanoscience and Nanotechnology

Over the past 10 years the word *nano* has become mainstream. *Nano* is being seen and heard in films, on the radio, on television, and in press. *Nano*material, *nano*-scale, *nano*science, *nano*technology, and *nano*fabrication are the key words of this new paradigm.

In the international system of units (SI), *nano* is the prefix used when multiplying a unit by 10^{-9}. When associated with SI length unit metre it denotes one billionth of a metre, i.e., 10^{-9} m, being the length of ten hydrogen atoms or five silicon atoms aligned. As you read this sentence your nails just grew 1 nm each; a human hair is about 10,000 nm wide, which is the smallest dimension we can see with the naked eye.

Figure 14.1 illustrates a length scale from micro- to nanometer dimensions. But what does it mean to have a nanometer scale? It means that the (nano)object has at least one dimension (height, length, depth) below 100 nm (1–100 nm). According to the number of dimensions not confined to the nanoscale, nanomaterials may be classified as 0D (nanoparticles), 1D (nanotubes, nanofilaments, and nanofibers), 2D (nanofilms and nanocoatings), and 3D (bulks).

On 29 December 1959, the Nobel Prizewinner for Physics, Richard Feynman, gave his classic talk *There's Plenty of Room at the Bottom* [1], where by the first time ever someone envisioned the possibility of manipulating atoms or molecules

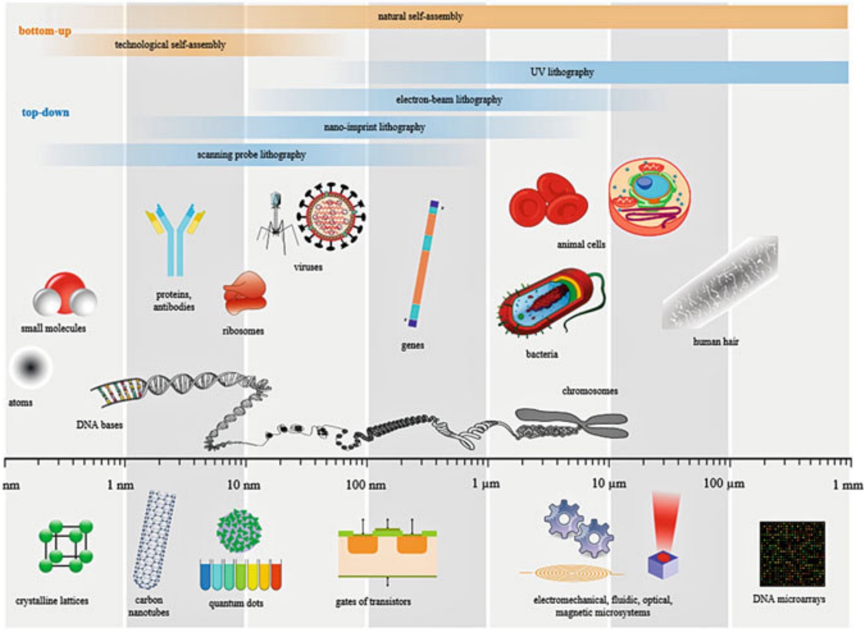


Fig. 14.1 Scale from micrometer to nanometer dimensions. Image Credits: http://upload.wikimedia.org/wikipedia/commons/2/29/Biological_and_technological_scales_compared-en.svg

Fig. 14.2 Air-bag motor, MEMS device. Image Credits: http://www.memx.com/products.htm

in order to fabricate new materials with unexpected, outstanding properties. New multidisciplinary research fields opened up and a wide range of new materials become available. The term nanotechnology was first used in 1974, by Norio Taniguchi, when referring to the accuracy and precision of tolerance in machinery, in a paper where a *top-down* approach to nanotechnology was disclosed [2]. Latter in 1986, K. Eric Drexler, describing the ultimate *bottom-up* approaches, used this term for the second time [3]. But how can nanotechnology be defined? Nanotechnology is all about the study and development of new functional artificial materials/systems whose structures and components exhibited novel and significantly improved physical, chemical, and biological properties, due to their *nano*scale size. It was necessary to wait until the development of powerful characterization techniques such as electron microscopy, scanning tunnelling microscopy, magnetic force microscopy, and atomic force microscopy to observe the bloom of nanotechnology in the last decade.

Today's interest in nanotechnology is driven by the semiconductor industry, which is constantly concerned about making devices smaller. Economic pressures in the electronic industry have forced the development of new lithographic techniques (a *top-down* approach) that continue the steady reduction in feature size and cost (Fig. 14.2). Electronic devices halve in size every 18 months (Moore's law [4] (Fig. 14.3)). Although this law was proposed to hold until the mid-1970s, it is still observed today!

But nanotechnology is not restricted to the electronics and semiconductors industry—medicine is an upcoming new customer. The use of nanotechnology in medicine (nanomedicine) is promising and has deeply attracted the academic, pharmaceutical, medical, and industrial communities, being an area of exponential growth [5]. Proteins, as an example, have been used to produce vaccines since the beginning of the twentieth century. But one of the most promising areas in *nano*medicine is *theranosis,* where treatment and diagnosis are accessed together

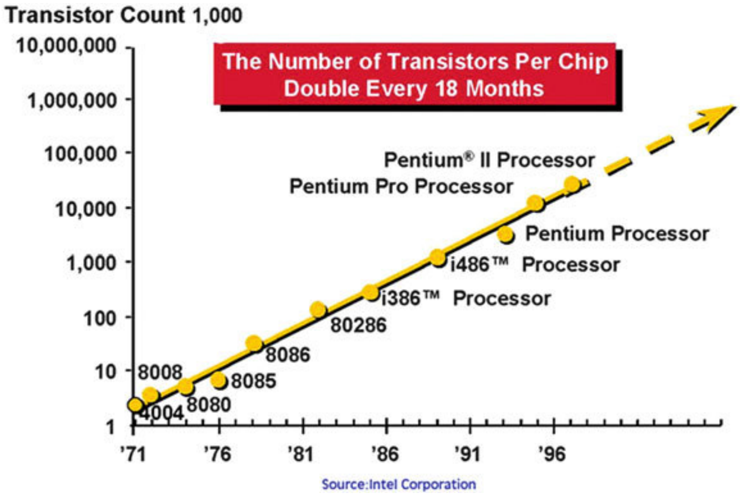


Fig. 14.3 Moore's law. Image Credits: http://www.intel.eu/

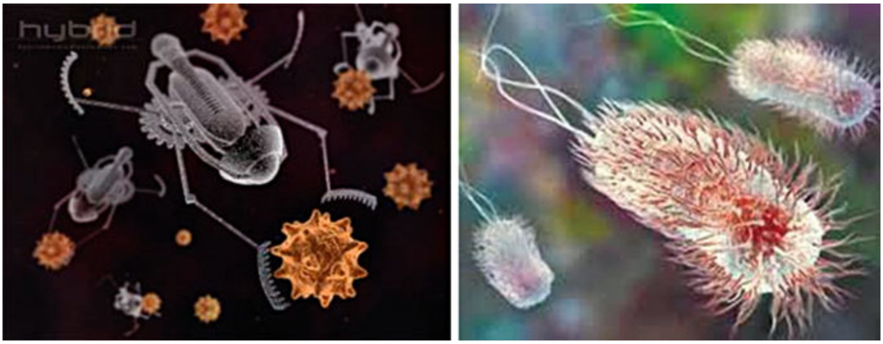


Fig. 14.4 Nanorobots for medicine. Image Credits: http://nanomedicine.yolasite.com; http://www.boolokamonline.net

(Fig. 14.4). *Theranosis* includes early diagnosis and targeted drug-delivery for cancer, biomedical instrumentation surgery, pharmacokinetics monitoring of diabetes and healthcare, just to mention but a few.

Photonic crystals devices, like lenses and bipolar transistors, have been developed with new amazing optical and optoelectronic properties [6, 7]. The discovery of new synthetic materials, such as fullerenes and carbon nanotubes [8], or nanostructured mesoporous silica [9, 10] (Fig. 14.5), have been enhancing nanotechnology.

But what makes nanotechnology so special? Firstly, it covers many fields, being an incredibly wide-reaching and interdisciplinary area—it demands skills in biology, physics, materials science, mechanical and electronic engineering and,

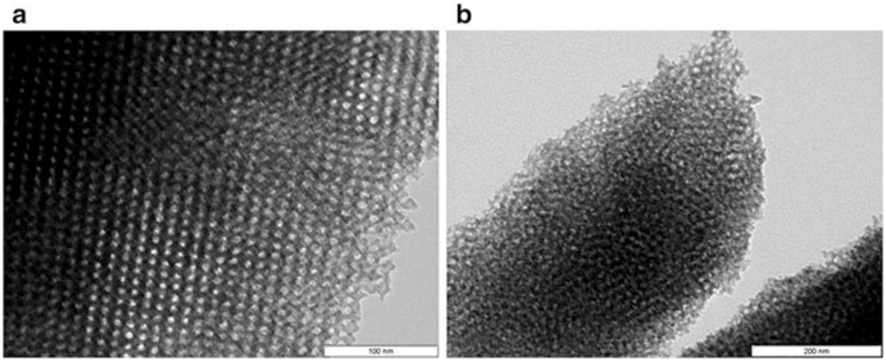


Fig. 14.5 Nanostructured mesoporous silica films: (**a**) lamellar domain Lα, (**b**) biphasic domain I_1+H_1 (M.C. Gonçalves and G. Attard, unpublished work)

sometimes, medicine. Secondly, nanotechnology it is an area which crosses the border between atoms/molecules and the macro world. Thirdly, it is the ultimate scientific quest where every structure and/or properties are design at a molecular level.

14.1.1 Nanotechnology in Art History

Although the concept of nanotechnology belongs to the present, the study of nanomaterials can be traced back for centuries, where some old technological processes led to the inclusion and/or formation of nanoparticles in the final product. At the time most of the phenomena were not understood, and knowledge of technology was based on experiments and trial and error. Glasses, for example, exhibiting extreme brilliance by the inclusion of colloidal quantum dots, have been known since ancient Rome. At the time quantum dots were fabricated by the mechanical formation of gold and silver dust nanoparticles. Gold nanoparticles were also used by the Chinese as an inorganic dye to color their porcelains red, more than 1,000 years. Colloidal solutions were formulated by Egyptian in 400 B.C. via 'alchemia.' Two centuries ago, Michael Faraday investigated the properties of colloidal gold and attempted to explain their ruby color. By adding a reducing gent to aqueous solutions of $NaAuCl_4$ a ruby-colored fluid forms. Faraday explained it by the presence of very finely divided gold particles dispersed in the aqueous solution, which was confirmed latter by electron microscopy (where Au nanoparticles of 6 nm average diameter were observed).

The second half of the third century and fourth century AD in Ancient Rome was a high time when it comes to cut glass production. *Lycurgus Cup* [11] (Fig. 14.6) is an iconic cage cup (*diatreta*) from that period. *Lycurgus Cup*'s color is pretty unusual—pea green in ambient light (reflected light) and magenta when illuminated from the inside (transmitted light). The presence of two colors in the glass work was

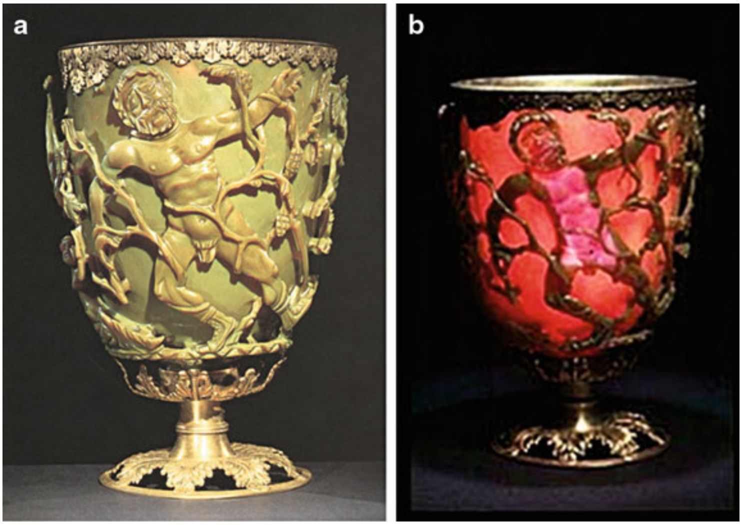


Fig. 14.6 *Lycurgus Cup's* color: (**a**) pea green under reflected light and (**b**) magenta under transmitted light. Image Credits: *Five Thousand Years of Glass*, ed. Hugh Tait, Published for the Trustees of the British Museum, by British Museum Press (1999)

first supposed to be accidental, caused by two differently colored types of glass on the glass blowing rod [11]. Today we know that the *Lycurgus Cup* contains both gold (at a concentration of 40 ppm [12]) and silver nanoparticles. The introduction of gold (Au^0) and silver (Ag^0) dust (like small particles ranging from a few millimetres to a few hundredths of a micrometre) into the glass molten bath, along with the long melting times and the furnace reductive atmosphere would have given rise to the production of metallic nanoparticles. The incapacity of chemical bond metals to the amorphous silica network would have led to metal nanoparticles precipitation. These metal nanoparticles may undergo plasmon excitation (oscillation of free electrons on the surface of the metallic nanoparticle). The *Lycurgus Cup* is nowadays a paradigm of nanomaterials and is an example, long before its time, of the surface plasmon phenomenon [12].

Roman gold glass (third century AD) is *a* kind o*f laminated glass*, where a thin sheet of gold (measuring a few hundredths of a micrometre) is tied in two sheets of glass (Fig. 14.7a). The technique was spread around the Arab world in the year 500. Syrian gold glass pieces survive until today, exhibiting the presence of a colloidal of gold nanoparticles (Au^0) dispersed in the silica glass matrix (Fig. 14.7b) [11].

The Mediaeval and Antique ruby color results from light scattering due to the presence of silica microparticles (SiO_2) and metallic gold (Au^0) nanoparticles dispersed in the silica glass matrix (Fig. 14.8) [12].

But all that glitters is not gold! The iridescent metallic shine of Mediaeval and renaissance metallic ceramic glazes (*luster*) is due to the presence of metallic tin (Sn^0), silver (Ag^0) and copper (Cu^0) nanoparticles in the glaze matrix [12]. After the first firing (ceramics *sintering*) a second glaze is prepared. The second glaze is

Fig. 14.7 Gold glass: (**a**) Roman glass, third AD and (**b**) Syrian glass, 500. Image Credits: *Five Thousand Years of Glass*, ed. Hugh Tait, Published for the Trustees of the British Museum, by British Museum Press (1999)

Fig. 14.8 Royal Gold Cup, 1370–1380, Tudor, England. Image Credits: British Museum

Fig. 14.9 Renaissance *luster* plate, 1470–1500, Valencia, Spain. Image Credits: Victoria and Albert Museum

formed by a powder mixture of copper, silver, and aluminosilicate minerals, which is brushed on over the first glaze. A second firing under strong reductive atmosphere takes place and the final piece finished with an amazing metallic shine. The luster was originated in the Middle East in the ninth century, and spread to Egypt and Spain, where it reached its golden period in the fifteenth century in Spain (Fig. 14.9) [11]. Metallic glaze is still used today and is one of the signature marks of the Wedgwood factory.

The French Mediaeval cobalt blue, found in stained-glass windows in French cathedrals, is due to the presence of metallic cobalt nanoparticles (Co^0) dispersed in the glass matrix (and incorporated as Bohemia cobalt oxide) (Fig. 14.10) [12].

Maya blue has been a challenge for art and technology (Fig. 14.11). Maya blue resists weathering, natural alkalis, oxidants, acids, biological agents, and even modern chemical solvents. Unlike European and Asian blues, based on cobalt and lapis lazuli, Maya blue is based on a local plant dye—the *indigofera* plant—used in pre-Columbian textiles to produce the color indigo. Pre-Columbian indigo, however, does not resist acids nor does it have the intensity and iridescence of Maya blue [12].

Maya blue has been shown to contain *palygorskite* (an aluminosilicate 1D and 2D nanostructured). *Palygorskite* and indigo leaves were mixed together, ground, and melted. Several metallic impurities in Mayan wall paintings were observed—iron (Fe^0), manganese (Mn^0), and chromium (Cr^0)—along with the presence of metal oxidised forms. Maya blue arises from the dispersion of light (which depends on the size and shape of the nanoparticles present) and color (attributed to the presence of chromophores, metallic oxides). Minor traces of nanoparticles could have a significant effect on optical properties through plasmon effects. Maya blue's huge resistance to corrosion seems to be associated with the nanostructure of the aluminosilicate *palygorskite*. The interesting properties of the final product come from a complex mix of several natural nanomaterials [12].

Fig. 14.10 Cobalt blue in Mediaeval-stained glass windows in French cathedrals

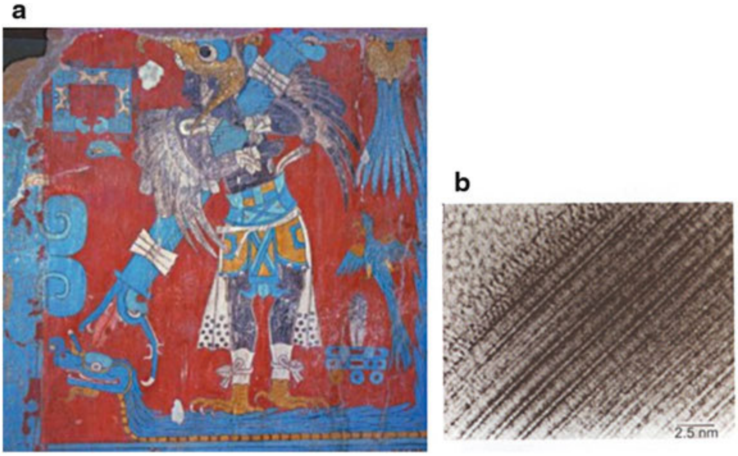


Fig. 14.11 Maya blue: (**a**) wall-painting Cacaxtla and (**b**) SEM image of *palygorskite*. Image Credits: *Nanomaterials, Nanotechnologies and Design. An Introduction for Engineers and Architects*, M. F. Ashby, P. J. Ferreira and D. L. Schodek, Elsevier (2009) (ISBN 978-0-7506-8149-0)

Mediaeval *frescoes* are an important European cultural legacy, particularly prevalent in Italy (Fig. 14.12). In the *buon fresco* technique, pigments mixed with water are applied on recently laid plaster, so the pigments impregnate the calcium carbonate structure. As well as esthetic quality and intense colors, *frescoes* are resistant to chemical and biological agents. Over time, however, the migration of salts through the porous structure of the carbonate (when damp) can produce crystals. Deterioration of the *fresco* can take place in the form of flaking [12].

Although the greatest artists of all time did not scientifically and technologically understand the chemical processes which brought about certain colors and optical effects, and did not know the concept of nanoparticles, trial and error has produced some truly remarkable works of art.

14.1.2 Nanomaterials in Nature

Life began on Earth 3.8 billion years ago. Since then, the different life forms have learnt to adapt to dynamic environmental conditions, some of which were extremely severe and toxic, and to reproduce. Nature is the most experienced laboratory ever, able to produce high performance materials, to convert different forms of energy, to self-repair and to store information in an exceptional efficient way. And a great deal of what nature does is done at nanoscale.

Throughout history we have tried to control nature but we do not notice the nano-engineering in the thousands of examples of natural products. In the nano-era we start looking at nature and mimicking natural products that emerged from millions of years of evolution.

Fig. 14.12 Fresco, Seasons, Castello del Buonconsiglio, Trento, Italy

Natural nanostructure materials aiming exceptional *high hardness* and *resilience* are found, for example, in mollusc shells. Warm-water abalone mollusc shell (Fig. 14.13a) is one of the most popular as it is twice as hard as the best high-tech ceramics around today. The abalone nanocomposite is made with stratified calcium

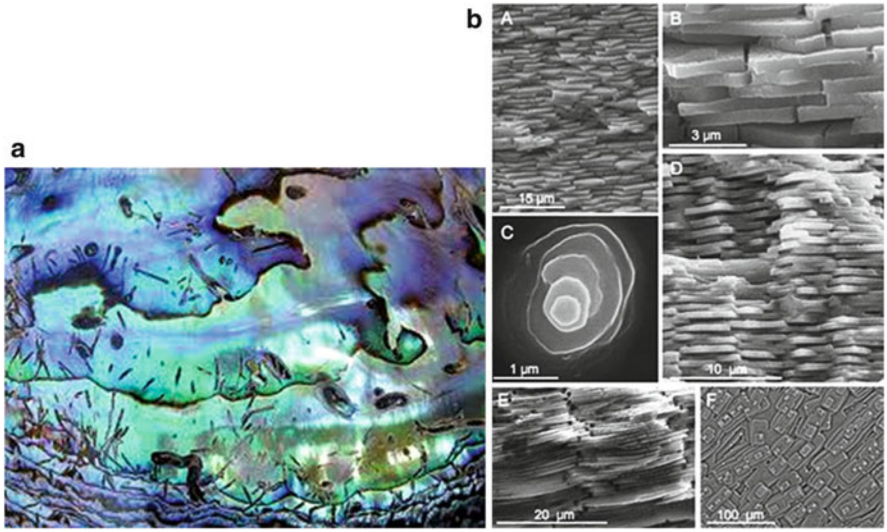


Fig. 14.13 Abalone (*Haliotis tuberculata*) shell (**a**). Different nacre microstructures found in mollusks (*A*, *B Pleiodon spekii*, *C*, *D Haliotis tuberculata, E*, *F Pinna nobilis* and *F* Nacre tablets observed from above) (**b**). Image Credits: www.flickriver.com; http://www.bioscience.org

carbonate ($CaCO_3$) plus a protein that acts like a binding agent (formed mainly of cysteine, histidine, and arginine) (Fig. 14.13b). The nanocomposite starts with the segregation of the protein by the mollusc and is followed by self-organization into a layered nanostructure. Between protein layers, precipitation of calcium carbonate crystals takes place (from the calcium and carbonate marine ions).

The reason for the abalone's excellent mechanical performance lies in its layered nanostructure. Under pressure, a crack in the shell (either internal or superficial) may spread throughout the fragile ceramic material but will be deflected as soon as it reaches the protein. Instead of a fragile material in which cracks would spread catastrophically until fracture, the abalone's shell is ductile and resilient [12].

Another example of *high mechanical resistant* natural nanostructured material is the rhinoceros horn. Rhinoceros horns are nanocomposites set up of keratin fibers (the fiber in hair and nails), 300 a 500 μm long, packed together (40 layers of cells), within a matrix also made of keratin (Fig. 14.14). Since the matrix and fibers are made of the same material, interfacial tension is low, leading to a rigid and with high tenacity material [12]. Mimicking this material has led to the production of nanofilaments and nanotubes in polymer/polymeric matrices.

We cannot fail to mention the thread of a spider web which is more *mechanically resistant* then kevlar fibre. The thread of a spider web is a natural water-insoluble nanocomposite with outstanding mechanical performance. Its structure is composed by polymer matrix (easily deformed) strengthened by (rigid) oriented nanocrystals. The polymer matrix provides its exceptional energy absorption

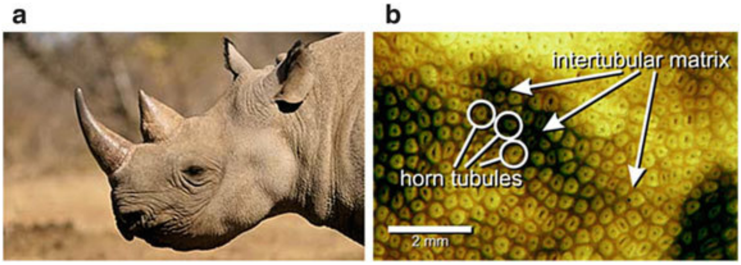


Fig. 14.14 Rhinoceros horn: (**a**) macro-scale and (**b**) micro-scale. Image Credits: *Nanomaterials, Nanotechnologies and Design. An Introduction for Engineers and Architects*, M. F. Ashby, P. J. Ferreira and D. L. Schodek, Elsevier (2009) (ISBN 978-0-7506-8149-0)

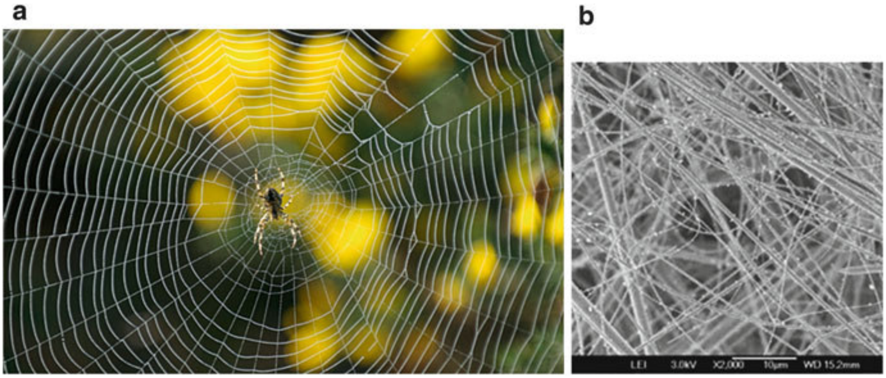


Fig. 14.15 Spider web: (**a**) macro-scale. (**b**) Manufactured glass nanofibers produce by laser spinning. Image Credits: http://www.per-forms.net

properties and the strengthening gives its outstanding mechanical resistance (Fig. 14.15a).

The strengthening of polyurethane elastomers with aluminosilicate nanoparticles (a synthetic nanocomposite) is one example of mimicking spider web fibers. Lightweight membranes and thin films with high mechanical resistance are some of the potential uses (Fig. 14.15b).

Biological *adhesion properties* are another source of inspiration. Geckos' feet are lined with a set of thin filaments (*setae*), 200 nm in diameter, ending in *nano shock absorbers (spatullas*). Each of these *spatullas* produces a very small adhesion force, 10^{-7} N, due to *van der Waals* interactions. Half a million *spatullas* (the estimated number per geckos) produce an adhesion force of 10 N [12]. The ability to adapt the filaments to surface topography and the heightened adhesion force allow the gecko to walk on ceilings or on smooth surfaces, such as the side of an aquarium. Mimicking this natural nanostructure drives to the production of patches of highly adhesive carbon nanotubes and polypropylene fibers (Fig. 14.16).

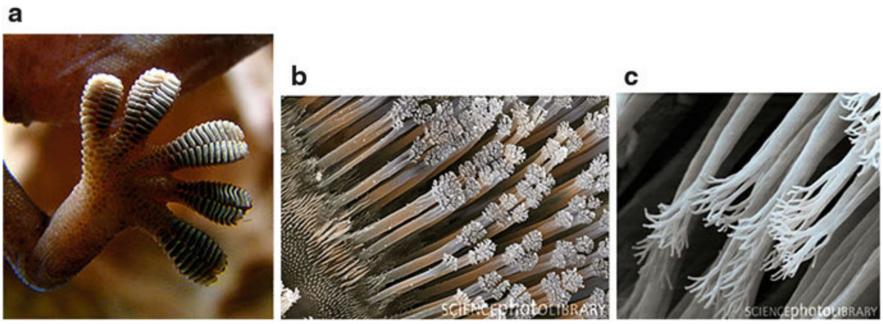


Fig. 14.16 Gecko's feet: (**a**) macro-scale and (**b**, **c**) micro-scale. Image Credits: Sciencephotolibrary

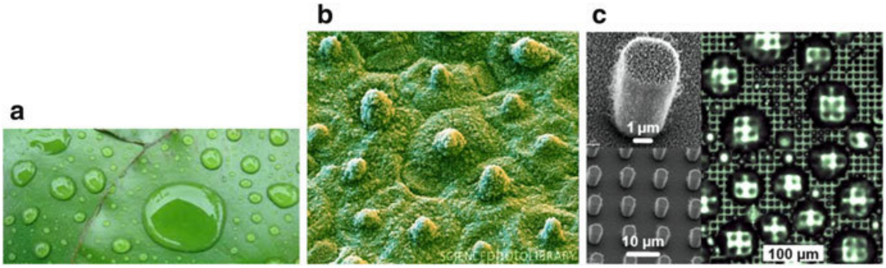


Fig. 14.17 Lotus leaf surface: (**a**) macro-scale, (**b**) micro-scale. Manufactured superhydrophobia surfaces (**c**). Image Credits: www.asknature.org; www.sciencephoto.com; http://www.asknature.org

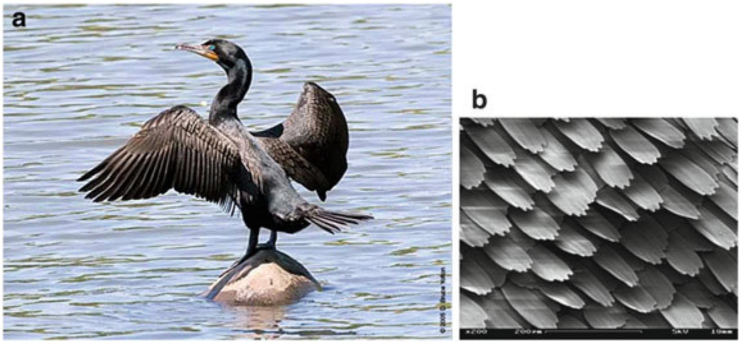


Fig. 14.18 Cormorant: (**a**) macro-scale and (**b**) micro-scale. Image Credits: Sciencephotolibrary

Another biological interesting property at nanoscale is *superhydrophobia*. The leaves of several plants show surface roughness at several different scales, which makes them superhydrophobic: the lotus leaf and the sponge are just two examples (Fig. 14.17a, b). The feathers of several birds reveal a nanostructure of nanospines and nanobarbs, which are also responsible for superhydrophobia (Fig. 14.18).

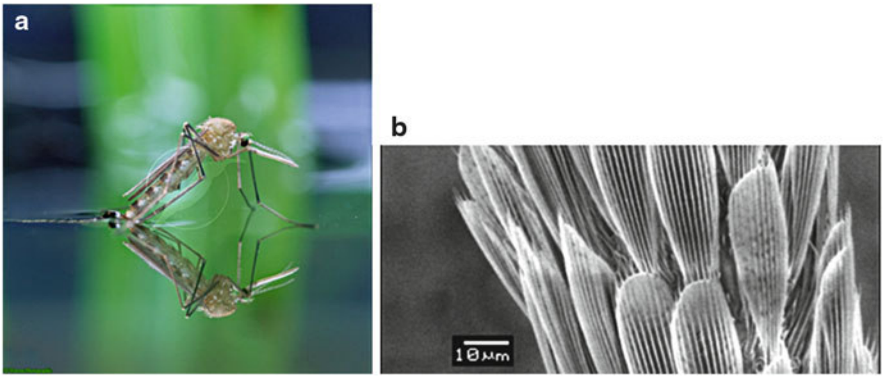


Fig. 14.19 Water skater: (**a**) macro-scale and (**b**) micro-scale. Image Credits: www.warrenphotographic.co.uk; www.asknature.org

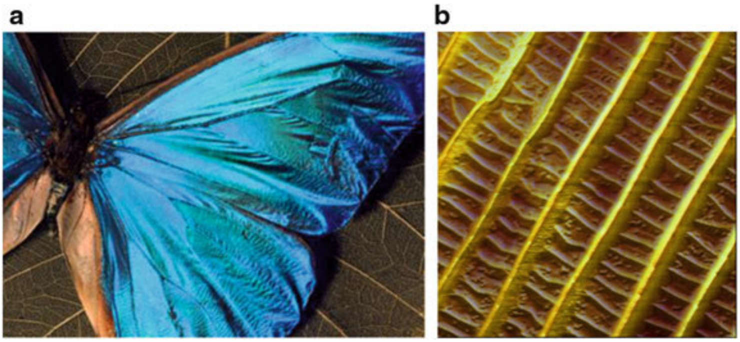


Fig. 14.20 Butterfly wings: (**a**) macro- and (**b**) micro-scale

The water skater is able to land or slide over the surface of water; its legs are lined with very fine hairs which end in nanonotches, making them superhydrophobic (Fig. 14.19). Mimicking these biological nanostructures allowed the production of man-made superhydrophobic materials (Fig. 14.17c).

Many other nanostructures have inspired engineering. The mimic of the nanoarchitecture of the iridescent butterfly wings or natural opal (Figs. 14.20 and 14.21) allowed the production of many photonic materials. A photonic crystal is a dielectric material with periodicity in its dielectric constant (or refraction index). Light transmission through the material is not, therefore, possible (due to Bragg's reflection) in a wavelength interval (known as stopband), based on a value of the order of size of the photonic structure's wavelength. Man-made opal, which is the result of nanospheres self-assembly, and inverse opal, which is the result of removing the motifs from the preceding *fcc* crystal, are two of the photonic nanocrystals produced using *bottom-up* methods (Fig. 14.22) [13, 14].

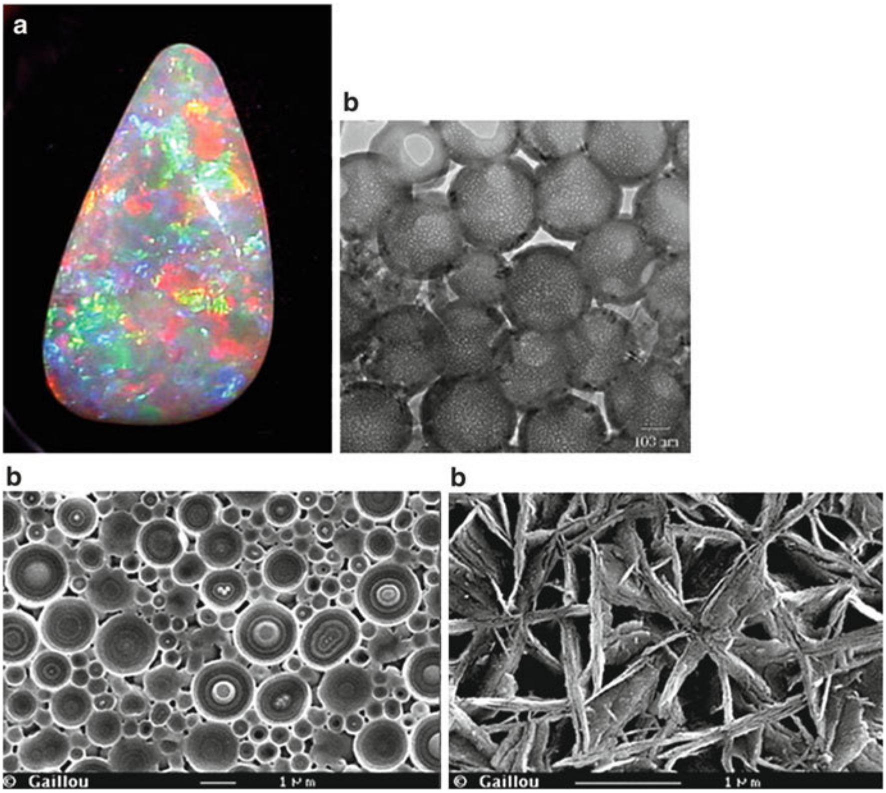


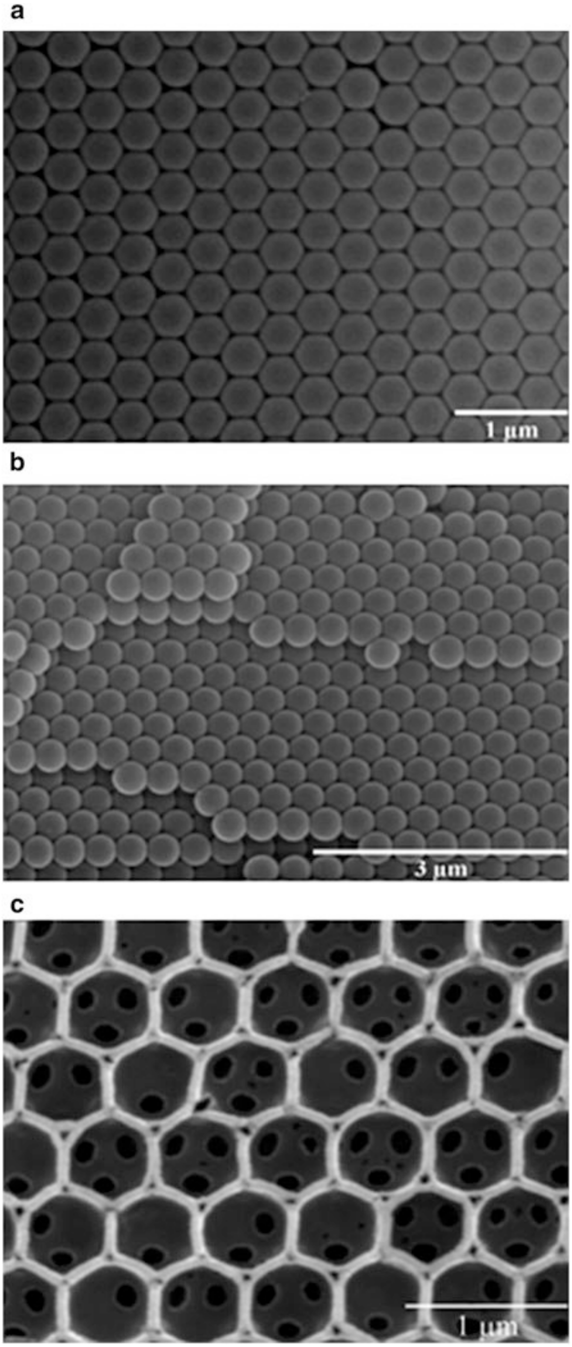
Fig. 14.21 Natural opal: (**a**) macro- and (**b**) micro-scale. Image Credits: NA Feoktistov, VG Golubev, JL Hutchison, DA Kurduykov, AB Pevtsov, VV Ratnikov, J Sloan and LM Sorokin, TEM and HREM study of 3D silicon and platinum nanoscale assemblies in dielectric opal matrix, *Semicond. Sci. Technol.* 16 (2001) 955 doi:10.1088/0268-1242/16/12/301

Another noteworthy property of natural materials is their ability for *self-healing*, essential for survival. Artificial materials rarely have this quality. The production of artificial materials able to, for example, repair cracks or restore qualities and/or functions is one of engineering's great challenges.

Bone is a complex organic material produced by an organic collagen matrix, strengthened with nanofibers which are also made of collagen, in turn strengthened by apatite nanocrystals. Collagen appears here as fibers of around 100 nm in diameter and 5–10 μm in length; apatite is composed of nanocrystals with thicknesses between 1.5 and 4.5 nm (Fig. 14.23). The strengthened collagen fibers are introduced into the collagen and apatite matrix.

The important property which comes out of this hierarchy is bone's ability to carry weight and absorb energy without breaking. Although the deformation mechanism is still not fully understood, the interface between the matrix and collagen fibers is able to break and reform under pressure, encouraging a repair mechanism at molecular level. The apatite nanoparticles are also protected against excessive weight.

Fig. 14.22 Artificial opal: (**a**, **b**) self-assembled polystyrene nanoparticles; (**c**) artificial inverse opal (M.C. Gonçalves, unpublished work)



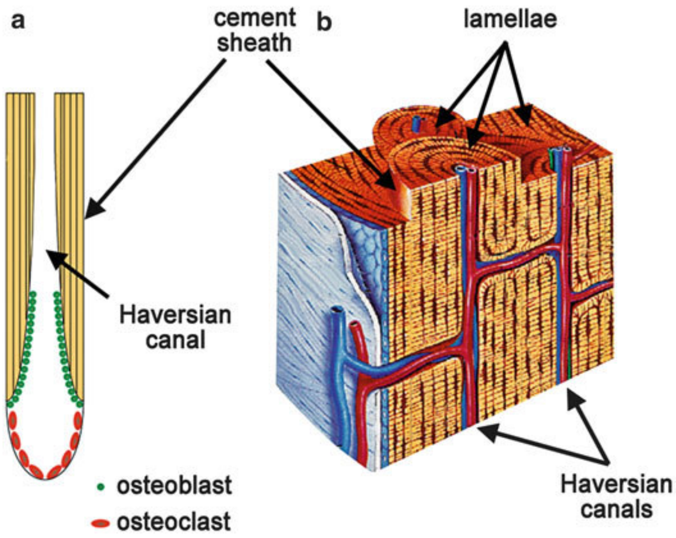


Fig. 14.23 Bone: (**a**) macro-scale and (**b**) micro-scale

Bones are also able to self-heal and are able to remove damaged parts and replace them with new tissue. A broken bone cuts the blood flow, which causes the cells to die. At this stage, the damaged area is removed, after which blood flow returns together with stem cells. Stem cells are the precursors for other cells, which are able to produce cartilage, fibrous tissue, and bone tissue [12].

Skin is another tissue which can self-heal. Self-healing begins with blood coagulation, which seals the wound, keeping chemicals and bacteria from entering. Later, a network of capillaries is formed, 8–10 μm in diameter, which are responsible for supplying nutrients and maintaining cell activity [12].

Self-healing materials have been developed based on these concepts. These materials contain micro- or nanoencapsulated curing agents and catalysts, in composite matrices. After breaking, the micro or nanocapsule is broken and releases the curing agent, which reacts with the catalyst, beginning the healing process (see *Building Materials with Self-Repairing Qualities*).

In addition to several nanoobjects inspired by the natural world which have already been produced, the possibility for new nanostructures and hierarchies are only limited by our imagination.

14.2 General Features of Nanomaterials

14.2.1 Size Matters

Nanostructures and nanomaterials possess a large fraction of surface atoms *per* unit volume. If one successively divides a macroscopic object into nanoscale, the ratio of surface atoms to interior atoms increases exponentially (Fig. 14.24). Let's

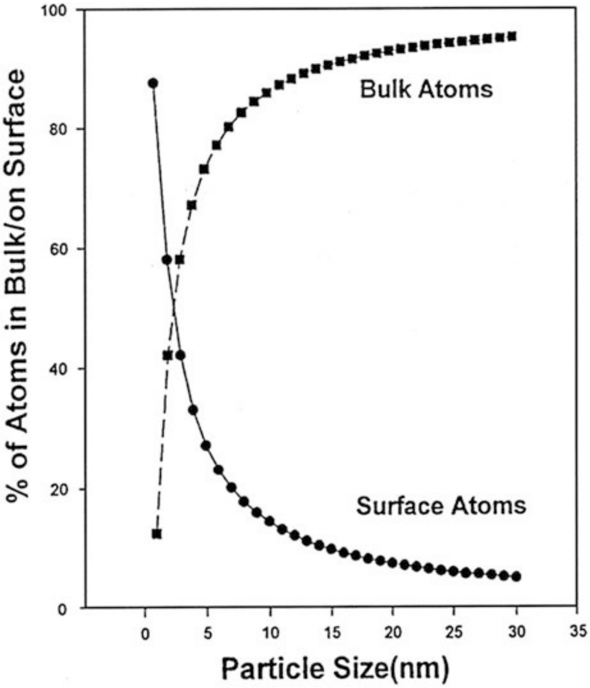


Fig. 14.24 Bulk/surface atoms function of particle size diameter

consider a spherical microparticle with 10 mm in diameter. If we now break it into several *nano*particles measuring 10 nm (in diameter) each, we will obtained 10^9 *nano*particles. The ratio of the *radii* is 10^3 while the ratio of the surface areas is 10^6, and the specific surface area is increased by a factor of 10^3! (The value of this estimate does not take into account the contraction caused by the reduction of surface tension.)

14.2.2 Shape Matters

When considering nanomaterials, shape must also be taken into account, since it contributes to the value of the specific surface area. It is the fact that nanomaterials' properties depend on *size* and *shape* (keeping constant the composition and the number of atoms/molecules) that gives them such great potential.

One of the main concepts in surface science and nanotechnology is the surface energy or surface tension, γ. In any material, bonds are affected by the formation of new surfaces, where some bonds are broken or modified. As a result, the average energy of the surface atoms will increase with the surface area.

Superficial energy is defined as the energy supplied to make a unit surface area, A, at temperature T, volume V, and chemical potential μ, constants:

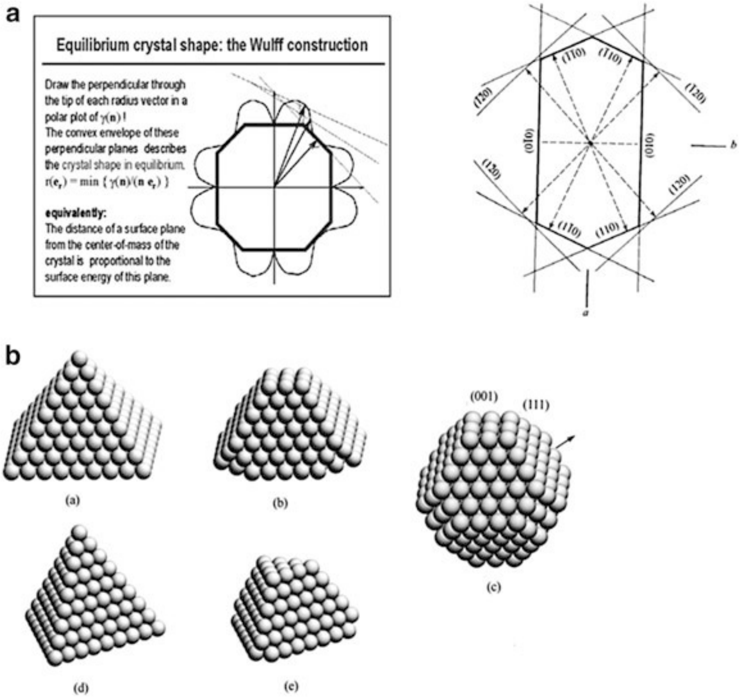
$$\gamma = (\partial H/\partial A)_{T,V,\mu} \tag{14.1}$$

where H is the Helmholtz's free energy.

Superficial energy is proportional to the number of interatomic bonds broken down at the surface, times the atomic planar density. In the case of crystalline solids, atomic planar density depends on the crystallographic plan, thus the surface energy.

In polycrystalline materials (or nanocrystals) the anisotropy is such that the equilibrium form of a crystal is determined by the superficial energy values of the different surfaces. The anisotropy of a crystal can be studied through the superficial energy γ's diagram.

If γ is isotropic, the equilibrium form is obviously a sphere. When γ is anisotropic, the equilibrium form is not a sphere, but a polyhedron. The precise polyhedron shape can be obtained through the Wulff diagram (Fig. 14.25).



Equilibrium crystal shape: the Wulff construction

Draw the perpendicular through the tip of each radius vector in a polar plot of $\gamma(\mathbf{n})$!
The convex envelope of these perpendicular planes describes the crystal shape in equilibrium.
$r(\mathbf{e}_r) = \min\{\gamma(\mathbf{n})/(\mathbf{n}\,\mathbf{e}_r)\}$

equivalently:
The distance of a surface plane from the center-of-mass of the crystal is proportional to the surface energy of this plane.

Fig. 14.25 Wulff diagram construction (**a**) and external shape of epitaxial particles (**b**): (**b**, **a**) (001) epitaxial particle with pyramid shape, (**b**, **b**) truncated (001) epitaxial particle, (**b**, **c**) Wulff polyhedron, (**b**, **d**) (111) epitaxial particle with regular tetrahedron shape, (**b**, **e**) truncated (111) epitaxial particle. http://www.k5.dion.ne.jp/~inos1936/shozoHP2E.html

14.2.2.1 Spherical Nanoparticles

One common shape of nanoparticles is spherical (the shape adopted by liquids and isotropic solid nanoparticles), since this is the shape which minimises the surface area to volume ratio.

For a sphere with a radius of r, the surface area is given by:

$$A = 4\pi r^2 \tag{14.2}$$

and the volume by;

$$V = \frac{4\pi r^3}{3} \tag{14.3}$$

Therefore the surface area to volume ratio is given by;

$$\frac{A}{V} = \frac{4\pi r^2}{\frac{4\pi r^3}{3}} = \frac{3}{r} \tag{14.4}$$

As the nanoparticle radius decreases, we get closer and closer to a critical value, after which the increase in surface area is extremely fast.

Knowing that many reaction phenomena take place on the interface, the increase in surface area will lead to a significant increase in the nanoparticle's reactivity.

14.2.2.2 Polyhedral Nanoparticles

For anisotropic crystalline solids, the shape taken on by the nanoparticles is not spherical but polyhedral. This can be observed in the initial phases of crystal growth (Fig. 14.26). In polyhedral nanoparticles (or nanocrystals) surfaces, edges and vertices exhibited different surface energy values.

Let us consider a certain crystalline material. From a thermodynamic point of view, the equilibrium shape of a crystal is determined by:

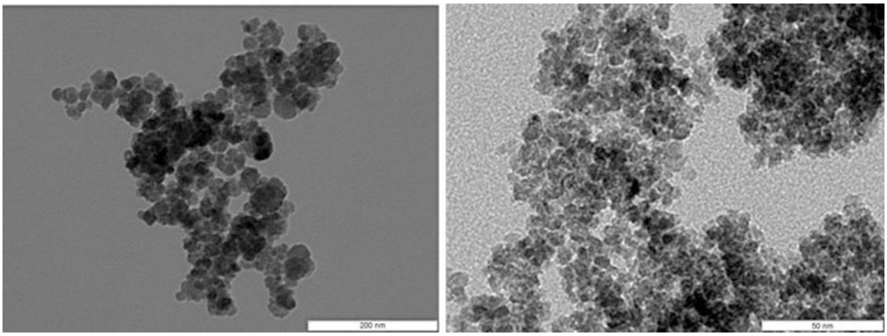


Fig. 14.26 TEM images of iron oxide nanoparticles, synthesized by co-precipitation in air. M.C. Gonçalves, unpublished work

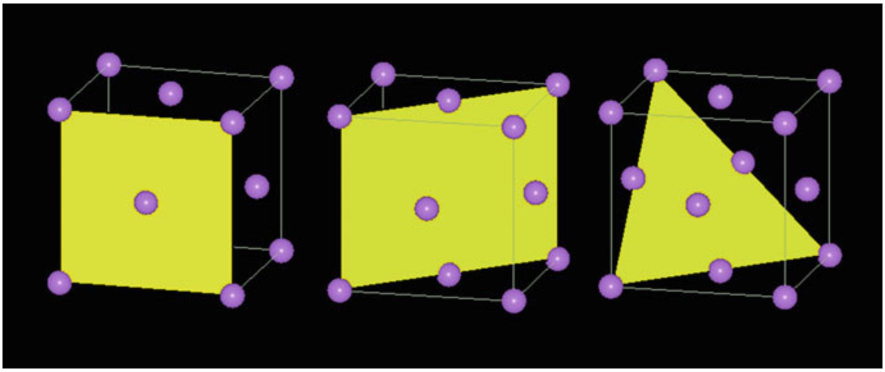


Fig. 14.27 {111} (**a**), {110} (**b**) and {100} (**c**) planes of the *cfc* structure [15]

$$\sum A_i\gamma_i = \text{Minimum} \tag{14.5}$$

in which γ_i is the surface energy of each face i, and A_i, the respective area.

Different crystallographic planes with different planar atomic densities will have different Gibbs free energy values. In the case of the *fcc* structure, the surface energy of highly symmetrical planes, {100}, {110} and {111} (Fig. 14.27), is given, respectively, by:

$$\gamma_{\{100\}} = \frac{4\varepsilon}{a^2} \tag{14.6}$$

$$\gamma_{\{110\}} = \frac{5}{\sqrt{2}}\frac{\varepsilon}{a^2} \tag{14.7}$$

$$\gamma_{\{111\}} = 2\sqrt{3}\frac{\varepsilon}{a^2} \tag{14.8}$$

And it is ordered in a monoatomic *fcc* crystal in the following way, $\gamma\{111\} < \gamma\{110\} < \gamma\{100\}$, unlike planar density, $\rho_{a\{111\}} > \rho_{a\{110\}} > \rho_{a\{100\}}$ [16].

The outer planes of a crystal (and, therefore, its polyhedral shape) can be determined theoretically (Wulff's theorem provides a quick method for showing how they are determined (Fig. 14.25)), minimizing the crystal's Gibbs energy. For an *fcc* structure of pure metals, the crystal shape, in thermodynamic equilibrium, is cubo-octahedral with 14 sides. It has 12 surface atoms and 1 inside atom (Fig. 14.28). It is important to stress that the shape of a crystal which grew in thermodynamic equilibrium cannot always be predicted theoretically.

Sometimes, above a certain temperature, the energy difference between the different planes is gradually lost, and the crystal becomes spherical rather than polyhedral. This temperature is known as the *roughening temperature*. If a particular crystal rises above the *roughening temperature*, it will produce a sphere rather than a polyhedron. Kinetic properties can also condition crystal shape.

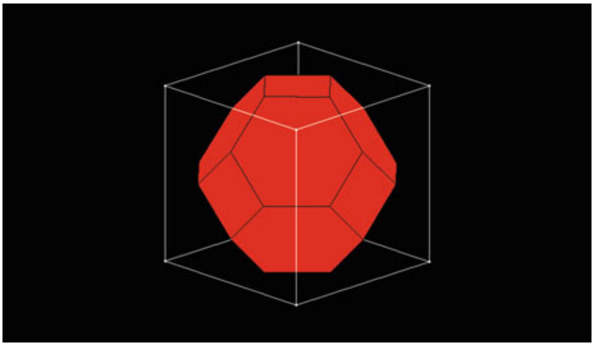


Fig. 14.28 Cube-octahedral structure in pure metal nanocrystals with *cfc* structure [15]

14.2.2.3 Magic Numbers

A set of chemically bonded atoms form a molecule. After a certain dimension threshold, instead of molecules they can be designated *nanoparticles*. Let us consider the formation of nanoparticles (with a single type of atoms), where the interatomic interactions are depicted by the Lennard-Jones potential:

$$V_{LJ}(r) = -2/r^6 + 1/r^{12} \tag{14.9}$$

where r is the interatomic distance.

As the number of atoms N increases, the geometric array varies. The atoms self-assemble in *clusters*, with defined geometries. When N is high enough, it is possible to have several geometric arrangements for the same N. For example, if $N = 6$, we witness two local minimums of Gibbs local energy—octahedral structure (stable) and tripyramide (metastable); if $N = 7$, the number of local minimums is 4. The number of local minimums grows rapidly with N, as Table 14.1 exhibits.

For each N, the Gibbs energy of the several local minimums (metastable) is close to each other, as well as to the absolute minimum of the system. The presence of different metastable states with energy values very close to each other suggests that the excess energy can be spread through different states; hence at fusion and solidification temperatures, different nanoparticles' forms may be present. During heating, the melting temperature is unique and defined thermodynamically. During cooling, solidification temperature differs from melting temperature.

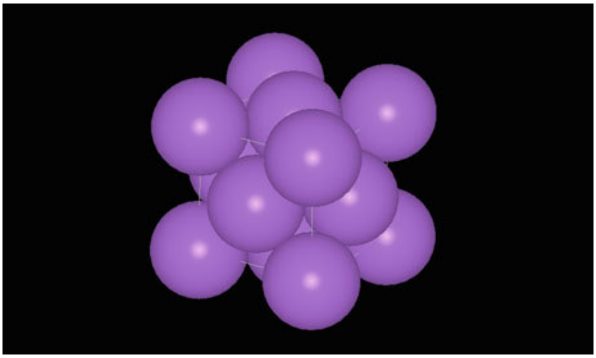
In *clusters* (and nanoparticles) the fusion temperature is inferior to the one observed in bulks. For big *clusters*, we witness another phenomenon. Not only does the fusion temperature (and the heat of the fusion) vary with nanoparticles size, it also varies according to their forms [16].

The *magical numbers* were first observed in 1980. *Magical numbers* correspond to predominant *clusters* (with a determined number of N atoms) in the production of pure metal nanoparticles, such as Na (monovalent), Cd, Zn (bivalents), Al (trivalent), and also in the transition metals (Cu, Ag, Au).

Table 14.1 Number of total energy local minimums in a particle of N atoms

N	6	7	8	9	10	11	12	13
	2	4	8	18	57	145	366	988

Fig. 14.29 *cfc* unit cell [15]



Let us consider gold (Au), silver (Ag), nickel (Ni), aluminium (Al), copper (Cu) or platinum (Pt), all face-centred cubic system (*fcc*) (Fig. 14.29). For a *cfc* nanocrystal with the size of a single cell, all (14) atoms are surface atoms.

When we add a layer of atoms to the *fcc* unit cell, the number of surface atoms becomes:

$$N^{\mathrm{S}}_{\mathrm{Total}} = 12n^2 + 2 \tag{14.10}$$

and the number of atoms inside becomes:

$$N^{\mathrm{I}}_{\mathrm{Total}} = 4n^3 - 6n^2 + 3n - 1 \tag{14.11}$$

Equations (14.10) and (14.11) show the number of surface and interior atoms of an *fcc* structure, depending on the number n of layers around the unit cell. These numbers are known as *magic numbers* and are shown in Table 14.2 [12].

As the crystal growth increases the percentage of surface atoms decreases. There is a boundary from which the number of surface atoms is a smaller fraction of the total number of atoms. This is the boundary between the nano and micro domains, where volume (or bulk) properties begin to prevail.

For a cube-octahedral structure (Fig. 14.28), the *structural magic numbers* are shown in Table 14.3 [12].

Carbon, for example, exhibited *clusters* with 60, 70, 180, 240, . . . 540, . . . atoms, being predominating the 60 and 70 forms (Fig. 14.30), named *fullerenes* according to the architect R. Buckminster Fuller, author of hexagonal and pentagonal *domes*. *Fullerenes* are allotropic forms of graphite (with sp^2 hybridization) and diamant (with sp^3 hybridization).

Table 14.2 *Magic numbers* for *cfc* structure

n	N^S surface atoms	N^I interior atoms	N^S/N^I	N^S (%)
1	14	0	–	100
2	50	13	3.85	79.3
3	110	62	1.78	63.9
4	194	171	1.13	53.1
5	302	364	0.83	45.3
6	434	665	0.665	39.4
7	590	1,098	0.535	34.9
8	770	1,687	0.455	31.3
9	974	2,456	0.395	28.3
10	1,202	3,429	0.350	25.9
100	120,002	3,940,299	0.0304	2.9

Table 14.3 *Magic numbers* for *cube-octahedral* structure

n	N^S surface atoms	N^I interior atoms	N^S/N^I	N^S (%)
2	12	1	12	92.3
3	42	13	3.2	76.4
4	92	55	1.6	62.6
5	162	147	1.1	52.4
6	252	309	0.8	44.9
7	362	561	0.6	39.2
8	492	923	0.5	34.8
9	642	1,415	0.4	31.2
10	812	2,057	0.39	28.3
100	98,000	3,280,000	0.029	3.0

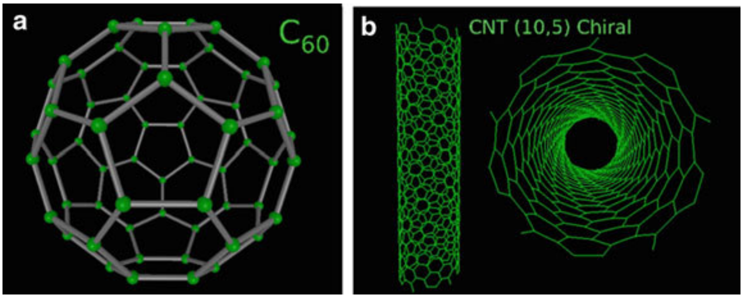


Fig. 14.30 Fullerene, C_{60} (**a**) and chiral carbon nanotube (**b**) [15]

With the size of the *cluster*, the possibility of having regular geometric forms increases. The most common are cuboctahedron, icosahedron, regular decahedron, star dodecahedron, truncated dodecahedron, and rounded dodecahedron.

In general, the nanoparticles fabrication processes that involve gas phases (see *bottom-up* approach) lead to the growth of nanoparticles in conditions out of thermodynamic equilibrium. For this reason, we witness a distribution of forms in the synthesized nanoparticles, since the energy between different metastable states is very close. In processes that involve colloidal synthesis, which kinetics is much slower, the form with the lower Gibbs free energy is, in general, favored.

As nanoparticles grow, internal tensions appear. They are eliminated through several mechanisms, such as dislocations, twinning, etc. When nanoparticles are heated, we witness a gradual variation of nanoparticle's shape (*see* Sect. 14.2.3).

When a *cluster* is composed by different chemical species (like in Ceramics), the difficulty in determining the nanocrystals' geometry increases, since the local charge balance must also be taken into consideration. For some compounds, the interaction of valence electrons can also interfere with the morphology and/or size of the nanocrystal. This is what happens, for example when forming aggregates (*clusters*) of potassium or erbium in glass matrixes [12].

14.2.2.4 Lattice Parameter

Real solids are finite. This is why the chemical environment around surface atoms is different from that around bulk atoms. The attractive forces which act on each bulk atom are isotropic, when observed over time. At the surface, atoms have some of their bonds broken, so their coordination number, CN (the number of closest neighbors), is lower than the CN of bulk atoms. The chemical environment around each surface atom is asymmetrical. This asymmetry submits surface atoms (or ions) to a force which works from the outside in; i.e., surface atoms are *pulled* towards the inside of the crystal. The length of chemical bonds involving surface atoms is smaller than chemical bonds involving bulk atoms (Fig. 14.31). The high surface/volume ratio of nanoparticles makes the number of chemical bonds involving surface atoms higher, meaning that the lattice constant is appreciably reduced [17].

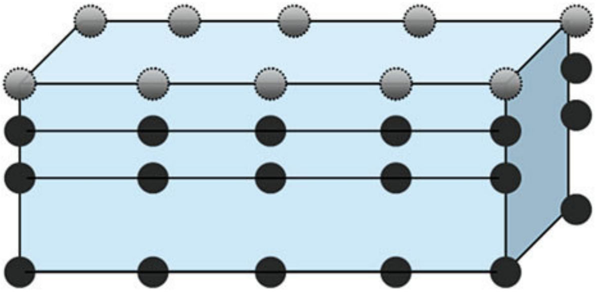


Fig. 14.31 Surface and bulk lattice constant

14.2.3 Physical Chemistry: Few Concepts

14.2.3.1 Homogeneous Nucleation and Growth

According to the Classical Nucleation Theory, which applies for supersaturated solution (or vapor) and supercooled liquid (or gas), when a liquid (or vapor) matrix/crystal nucleus interface is formed, with interfacial energy γ, for spherical nuclei with a radius r, the decrease of volume energy, $\Delta\mu_{\mathrm{V}}$, is described by:

$$\Delta\mu_{\mathrm{V}} = \frac{4}{3}\pi r^3 \Delta G_{\mathrm{V}} \tag{14.12}$$

where ΔG_{V} represents the volumetric Gibbs energy change. However, this energy reduction is counter-balanced by an increase in the surface energy, given by:

$$\Delta\mu_{\mathrm{S}} = 4\pi r^2 \gamma \tag{14.13}$$

being the overall change in Gibbs free energy of the system, ΔG:

$$\Delta G = \Delta\mu_{\mathrm{V}} + \Delta\mu_{\mathrm{S}} = \frac{4}{3}\pi r^3 \Delta G_{\mathrm{V}} + 4\pi r^2 \gamma \tag{14.14}$$

Figure 14.32 schematically shows the change of volume free energy, $\Delta\mu_{\mathrm{V}}$, surface free energy, $\Delta\mu_{\mathrm{S}}$, and total free energy, ΔG, as function of nucleus' radius. At the critical size $r = r^*$, ΔG will go through a maximum, $d\Delta G/dr = 0$. The critical size, r^*, and the critical energy, ΔG^*, may be defined by:

$$\Delta G^* = 16\pi\gamma^3/\left[3\Delta G_{\mathrm{V}}^2\right] \tag{14.15}$$

$$r^* = -2\frac{\gamma}{\Delta G_V} \tag{14.16}$$

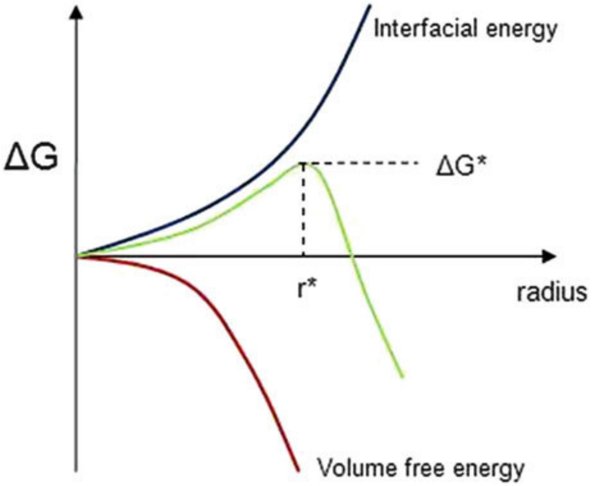


Fig. 14.32 Schematic change of volume free energy, $\Delta\mu_{\mathrm{V}}$, surface free energy, $\Delta\mu_{\mathrm{S}}$, and total free energy, ΔG, as function of nucleus' radius

where ΔG^* is the energy barrier that nucleation must overcome, and r^* represents the minimum size of a stable spherical nucleous. The newly formed nucleus is stable and continues to grow bigger only if its radius equals or exceeds a critical size, r^*. When the nucleus is smaller than r^*, it will dissolve into the solution to reduce the overall free energy.

In the synthesis of nanoparticles by nucleation from supersaturated solution (or vapor), this critical size represents the limit on how small nanoparticles can be synthesized. To reduce the critical size (and free energy), one needs to increase the change of Gibbs free energy, ΔG_V, and reduce the surface energy of the new phase, γ. For the synthesis of monosized nanoparticles, it is desirable that all nuclei form at the same time, i.e., nucleation should occur in a very short period of time.

14.2.3.2 Heterogeneous Nucleation and Growth

Homogeneous nucleation occurs in volume (3D), randomly, and spontaneously, without the presence of any preferential nucleation sites. Homogeneous nucleating systems are nevertheless uncommon. Most of the nucleation processes develop at *nucleation sites*, i.e., on preexisting surfaces contacting the liquid (or vapor), such as the surface of an impurity, a nucleating agent (a deliberately added nano/micro-crystal), crucible walls, etc. Suspended particles or minute bubbles also provide nucleation sites. The nucleation process is then designated by heterogeneous nucleation.

Let us consider the film deposition on a planar solid substrate. The growth species in the vapor phase impinge on the substrate surface, diffuse and aggregate to form a nucleus with a cap shape as illustrated in Fig. 14.33. Analogous to homogeneous nucleation, there is a decrease in the Gibbs free energy and an increase in surface or interface energy, given by:

$$\Delta G = a_3 r^3 \Delta\mu_v + a_1 r^2 \gamma_{vf} + a_2 r^2 \gamma_{fs} - a_2 r^2 \gamma_{sv} \tag{14.17}$$

where r is the average radius of the nucleus, $\Delta\mu_V$ is the change of Gibbs free energy per unit volume. The γ_{vf}, γ_{fs}, γ_{sv} are the surface (or interface energy) of vapor–

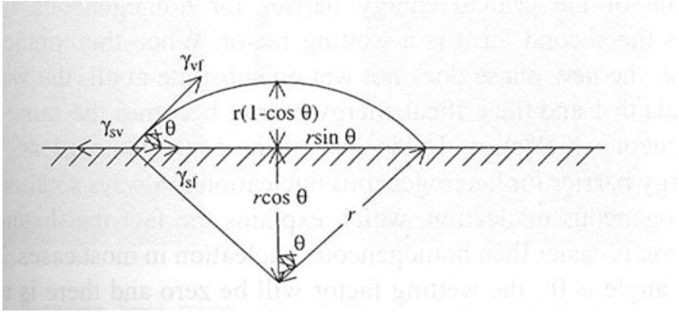


Fig. 14.33 Geometric constraints of heterogeneous nucleation. Image Credits: http://soft-matter.seas.harvard.edu/index.php/Contact_angle

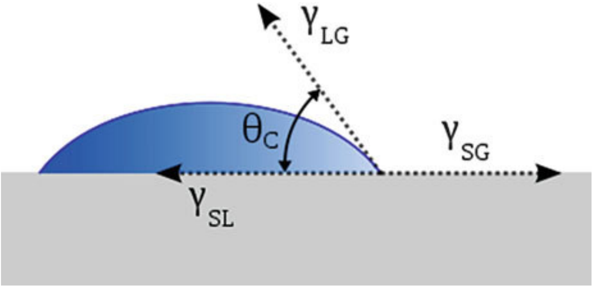


Fig. 14.34 Contact angle between a liquid (or vapor) deposited on a substrate. Image Credits: adapted from [17]

nucleus, nucleus–substrate, and substrate–vapor interfaces (Fig. 14.34), respectively, being related according to the Young's equation:

$$0 = \gamma_{SG} - \gamma_{SL} - \gamma_{LG} \cos\theta \tag{14.18}$$

where θ is the contact angle.

In heterogeneous nucleation, cap geometry (Fig. 14.34) allows some geometric constraints. After rearranging [18], one may obtain the critical radius and the critical energy barrier for heterogeneous nucleation:

$$r^* = \frac{2\pi\gamma_{\mathrm{vf}}}{\Delta G_{\mathrm{v}}}\left\{\frac{\sin^2\theta\cos\theta + 2\cos\theta - 2}{2 - 3\cos\theta + \cos^3\theta}\right\} \tag{14.19}$$

$$\Delta G^* = \left\{\frac{16\pi\gamma_{\mathrm{vf}}^3}{3(\Delta G_{\mathrm{v}})^2}\right\}\left\{\frac{2 - 3\cos\theta + \cos^3\theta}{4}\right\} \tag{14.20}$$

The first term of Eq. (14.20) is the value of the critical energy barrier for homogeneous nucleation (Eq. (14.15)), whereas the second term is a wetting factor.

But other factors, such as the interaction between the film and the substrate, may play a critical role on the film growth mechanism. Three different nucleation mechanisms may develop: island or Volmer-Wever growth; layer or Frank-van der Merwe growth and island-layer or Stranski-Krastonov growth (Fig. 14.35).

One may then summarize the film growth mechanism as follows:

- When the *contact angle is 0°*, the deposit wets the substrate completely, there is no energy barrier for the formation of a new phase and a *layer growth mechanism* is observed (Fig. 14.35). A first complete layer is formed, before the deposition of second layer starts. In the *layer growth mechanism*, the growth species are stronger bonded to the substrate than to each other. Epitaxial growth of single crystal films is one of the examples.
- When the *contact angle is less than 180°* (but *larger than 0°*), the energy barrier for heterogeneous nucleation is smaller than that for homogeneous nucleation, being the reason for the predominance of heterogeneous nucleation. An *island growth mechanism* frequently developed (Fig. 14.35). Here the growth species

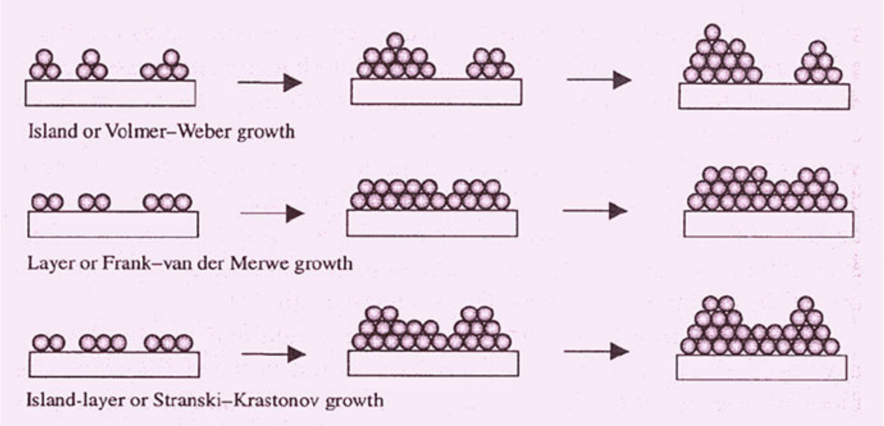


Fig. 14.35 Island or Volmer-Wever growth; layer or Frank-van der Merwe growth and island-layer or Stranski-Krastonov growth mechanisms. Image Credits: adapted from [17]

are more strongly bonded to each other than to the substrate. In the initial steps small islands form, and the subsequent growth will occur by their coalescence to form a continuous film. Systems of metals deposited on insulator/alkali halides/graphite/mica substrates exhibited this nucleation mechanism during the initial film formation.

- When a *strong mismatch* (see mismatch) is observed between the film and the substrate (for a *contact angle less than 180°*, but *larger than 0°*) an *island-layer mechanism* will occur (Fig. 14.35). The development of in situ stress in the film is the common reason for the *island-layer growth* mechanism.
- When the contact angle is 180° (i.e., the film does not wet on the substrate at all) the wetting factor becomes 1, the nucleation is homogeneous (i.e., the critical energy barrier for heterogeneous nucleation equals that of the homogeneous nucleation).

14.2.3.3 Lattice Mismatch or Misfit

Epitaxy is the formation of a single crystal on a single crystal substrate. Epitaxial growth can be further subdivided in (1) homoepitaxy and (2) heteroepitaxy. (1) In homoepitaxy the deposited film has the same crystal structure and chemical composition as that of the substrate, so no lattice mismatch is present; (2) in heteroepitaxy although the deposited film has a close matching crystal structure to the substrate, the film composition is different and a lattice mismatch developed.

Lattice mismatch or misfit is defined by:

$$f = \frac{a_\mathrm{s} - a_\mathrm{f}}{a_\mathrm{f}} \tag{14.21}$$

where a_s and a_f are the unstrained lattice parameters of the subtract and of the film, respectively. If $f > 0$, the film is strained in tension, whereas if $f < 0$, the film is strained in compression. Strain energy, E_s, develops in strained films (see Sect. 14.2.3.2),

$$E_s = 2\mu_f \left(\frac{1+v}{1-v}\right)\varepsilon^2 hA \qquad (14.22)$$

where μ_f is the shear modulus of the film, ν the Poisson rate's ratio, ε, the planar or the lateral strain, h, the thickness, and A the surface area. The strain energy increases with the film thickness.

14.2.3.4 Thermodynamic Stability, Instability, and Metastability

One of the fundamental differences between nano- and micro-scale materials (or macro) is the fact that nanoscale surface areas reach remarkable values. At nanoscale the high surface energy gives materials thermodynamic instability or metastability. To produce and stabilize nanomaterials or nanostructures, we must beat this very high surface energy.

A system is said to be in thermodynamic equilibrium when it is at its lowest energy state, which corresponds to the minimum of function G (A in Fig. 14.36), or, mathematically,

$$dG = 0 \qquad (14.23)$$

In A, small variations in atomic arrangement will not produce variations in G.

However, there are configurations in which although Eq. (14.23) is true, they do not correspond to absolute minimums but rather to local energy minimums in the system (situation B in Fig. 14.35). These configurations are known as *metastable* [18].

Configurations for which $dG \neq 0$ are known as unstable and correspond to very short events.

The Gibbs free energy calculation always considers a perfect, infinite crystal. Surfaces, grain boundaries, and interfaces are also not included. However, real

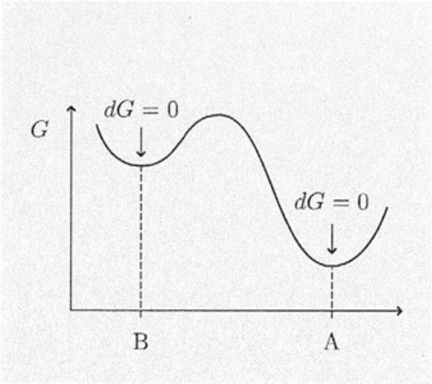


Fig. 14.36 Gibbs free energy of a system: A—thermodynamic equilibrium and B—metastable equilibrium

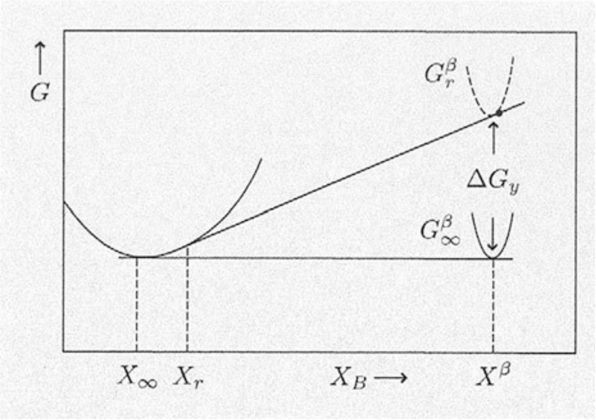


Fig. 14.37 Gibbs-Thomson effect

crystals have these discontinuities as well as line and point defects. For this reason, the thermodynamic equilibrium of a real crystal (finite and with defects) can only be achieved when all the interfaces, dislocations and impurities are eliminated (as vacancies are in thermodynamic equilibrium!).

The contribution of interfaces is particularly relevant in the first stages of crystal growth (through precipitation, segregation, etc.) of a β-phase (at nanoscale) at the heart of α matrix. This is why nanoparticles are metastable structures and do not correspond with the lowest Gibbs free energy situation. The solubility of the β-phase in α matrix also depends on the size of the nanoparticle, which is known as the Gibbs-Thomson effect (Fig. 14.37) [18].

14.2.4 Motivation to Growth

One of the great challenges in fabrication and processing of nanomaterials is to overcome the surface energy and to prevent the nanostructures and nanoparticles from agglomeration or growth in size, driven by the reduction of overall surface energy.

The reduction of surface energy is the driving force behind surface relaxation or restructuring, oxidation or passivation, physical or chemical absorption, compositional segregation, the formation of faceted (rather than nanospherical) nanocrystals, sintering (when around ambient temperature), Ostwald ripening, or agglomeration. All these mechanisms allow the surface energy of nanoparticles, nanostructure, or nanosystems to be reduced.

14.2.4.1 Ostwald Ripening

When two particles with different radii ($R_1 \gg R_2$) are dissolved or suspended in a liquid, each particle will develop equilibrium with the liquid. According to Kelvin equation, the smaller particle will have a higher solubility. Consequently, the solute will diffuse from the environment closer to the smaller particle to the environment

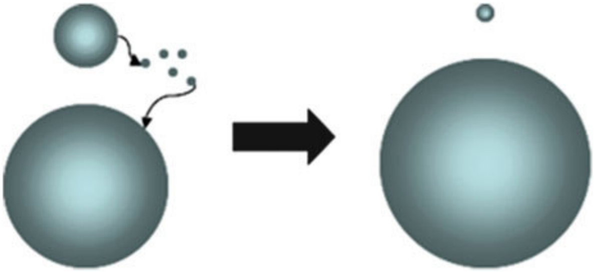


Fig. 14.38 Ostwald ripening

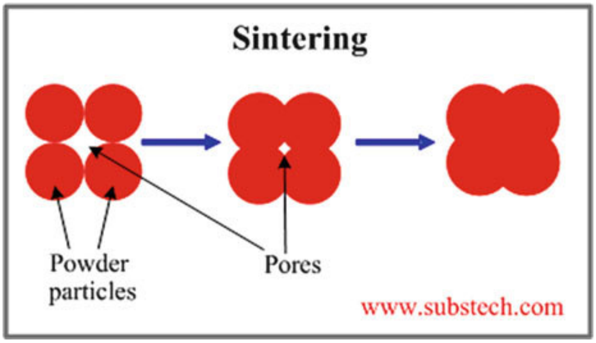


Fig. 14.39 Sintering

closer to the larger particle. To keep the thermodynamic equilibrium, solute will deposit onto the surface of the larger particle. To compensate the solute diffused away the smaller particle will continue dissolving. As a result, the small particle gets smaller, whereas the large particle gets larger (Fig. 14.38).

Ostwald ripening is an expontaneous process, quite useful in narrowing nanoparticles size distribution, and can be promoted by varying process temperatures.

14.2.4.2 Sintering

To preserve nanoparticles (after synthesis) sintering must be avoided. Sintering is a complex process that involves solid-state diffusion, evaporation-condensation or dissolution-precipitation, viscous flow, and dislocation creep and can occur at quite low temperatures when nanoparticles are present. Sintering promotes the replacement of solid-vapor by a solid–solid interface through reshaping of nanoparticles, promoting higher efficient packing of the nanocrystals (Fig. 14.39).

14.2.4.3 Surface Relaxation and Restructuring

One of the mechanisms responsible for surface energy reduction is surface relaxation, where the surface atoms shift inwardly. Surface relaxation is more common in liquids than in solids due to its rigid structure (*see* Sect. 14.2.2.4).

Surface restructuring occurs through the combination of surface dangling bonds into stained new chemical bonds.

14.2.4.4 Oxidation and Passivation

Surface adsorption takes place through chemical or physical adsorption of chemical species onto the surface by forming chemical or physical bonds.

Oxidation and passivation are special surface adsorption cases, where the surface atoms bound to oxygen, forming a surface (protective) film.

14.2.5 Scales Law

Small features permit more functionality in a given space, but nanotechnology is not only a scale down process from micron to nanometer scale. Materials in the microscale regime mostly exhibit the same physical properties as that of bulk form; nevertheless, materials in the nanometer scale may exhibit remarkable specific physical, chemical, or biological properties.

14.2.5.1 Gravitational Force Versus van der Waals Force

Let us consider an object with mass m and characteristic length L. The area is a function of L^2

$$S \approx L^2 \tag{14.24}$$

the volume, of L^3

$$V \approx L^3 \tag{14.25}$$

and the mass, of L^3

$$m \approx L^3 \tag{14.26}$$

Let us now consider the object under the influence of a gravitational field. The force of gravity is one of the greatest on the earth's surface, given by $F_g = mg$, where g is the acceleration of gravity, which means

$$F_g \approx L^3 \tag{14.27}$$

The pressure exerted by a body on the ground is calculated by $P_g = F_g/S$, which means

$$P_g \approx L^3/L^2 = L \tag{14.28}$$

At microscopic level, however, adhesion forces cannot be underestimated. Let us consider, then, adhesion between two surfaces through *van der Waals* forces $F_{\text{vdW}}(x)$ (main adhesion force for distances x between 2 and 10 nm). $F_{\text{vdW}}(x)$ is proportional to contact area, which means

$$F_{\mathrm{vdW}}(x) \approx L^2 \tag{14.29}$$

Since F_g and F_{vdW} vary differently with L, its ratio is dimensional and a function of L

$$F_{\mathrm{vdW}}/F_g \approx L^{-1} \tag{14.30}$$

At microscopic level, adhesion force takes precedence over gravitational force. The critical value for which gravitational force and adhesion force have equal intensity is a function of x and the nature of the medium between the two surfaces. For values of $L < 1$ mm, F_g is less than F_{vdW}. The gravitational force is therefore negligible at micro and nanoscales [16].

14.2.5.2 Friction Forces

When one surface slides over another, friction takes place F_f which acts against the movement. Friction force gets lower as the roughness of the surfaces in contact with each other decreases, and as the adhesion between surfaces decreases.

At macroscopic level, F_f is independent of the contact area (surface area where sliding takes place), since it is considered that two rough surfaces have few contact points. Friction forces are defined by $F_f = \mu F_g = \mu mg$, where μ é is the friction coefficient.

For constant m,

$$F_f \approx L^3 \tag{14.31}$$

At micro-scale, interatomic forces, although not reaching far, are intense and responsible for the increase in contact points between sliding surfaces—now adhesion between the surfaces cannot be ignored. The friction force at micro-scale, F_s, contains the friction and adhesion, and therefore becomes a function of the contact area

$$F_s \approx L^2 \tag{14.32}$$

This relationship is valid for small L (a few nm), while the relationship [17] is valid for higher values of L (>a few tens of nm). It is not, however, possible to establish a value for L, for which F_s and F_f are the same order of magnitude. Parameters such as the roughness of the surface in contact or the resistance of the materials under pressure are some of the determining parameters. At nanoscale, however, F_s is definitely predominant [16].

14.2.6 Size-Dependent Properties

Although micromaterials are used every day, they do not generate the interest which nanomaterials do. The reason for this is that micromaterial properties are essentially bulk properties. The nanolevel represents the overlap between traditional physics and quantum mechanics. At this scale the physical, chemical, and biological properties of materials differ in fundamental ways from the properties of either individual atom or bulk matter. This makes the prediction of cause and effect relationships much more difficult and introduces phenomena such as quantum tunnelling, superposition, and entanglement. As a result, material at the nanoscale can exhibit surprising characteristics that are not evident at large scales.

Crystalline structures present in macromaterials are also present at nanoscale, but ferroelectric and ferromagnetic materials can lose their ferroelectricity and ferromagnetism when they are reduced to nanoscale (which is what happens to copper nanoparticles with sizes below 70 nm, or iron nanoparticles below 15 nm). Conductors and semiconductors can become insulators when one of their characteristic dimensions is in the order of nanometres (copper is one of these examples). Carbon atoms in the form of a nanotube exhibit tensile strengths 100 times that of steel and can be either metallic or semiconducting depending on their configuration. Solid gold does not show catalytic properties but Au nanocrystals are excellent catalysts at low temperatures (when their radius is equal to or smaller than 5 nm). Gold and CdSe nanoparticles can appear orange, purple, red, or greenish, depending upon the specific size of particles (Fig. 14.40). The melting point for nanocrystals is significantly lower than that of solid gold (the decrease can be up to 1,000 °C! (Fig. 14.41)). Gold's melting point (in bulk) of 1,064 °C falls to 750–800 °C for

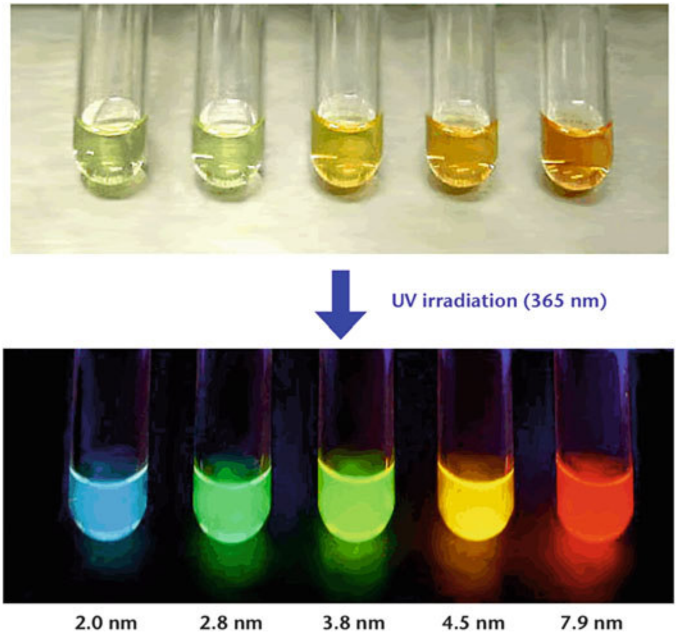


Fig. 14.40 Size effect on photoluminescence wavelength of CdSe nanoparticles (λ_{ex}: 365 nm). Image Credits: http://www.scl.kyoto-u.ac.jp; Chem. Lett. 2005, *34*, 1004

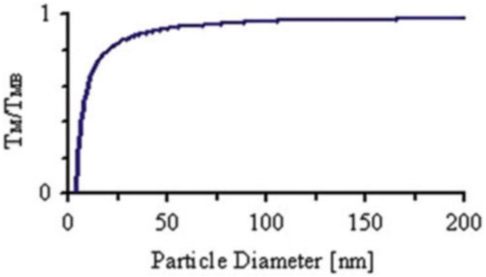


Fig. 14.41 A normalized melting curve for gold as a function of nanoparticle diameter. The bulk melting temperature and melting temperature of the particle are denoted T_{MB} and T_{M}, respectively (adapted from [19]). Image Credits: adapted from [19]

nanoparticles of 5 nm. The lattice constant can fall, and even the material's color can change depending on nanodispersion (for example, gold nanoparticles can appear orange, purple, red, or greenish, depending upon the specific size of particles) [12, 16, 17]. Titanium dioxide and zinc oxide, common ingredients in sun screen, both appear white when made of macro particles, but become translucent when ground to the nanoscale.

14.2.7 *Top-down* and *Bottom-up* Approaches

Producing nanomaterials is an enormous technological challenge. The state of minimum Gibbs free energy of a material corresponds to a perfect monocrystal. Its subdivision into smaller nanocrystals is responsible for a surface area and energy increase, difficulting production and maintenance. The most common methods for the fabrication of structures in the submicrometer size regime are the *top-down* ('from large to small' *or step-wise design*). *Top-down* technology is based on lithographic techniques, where nanoscaled elements are cut from larger entities. In the *top-down* method, structures and/or mechanisms are miniaturized to the nanoscale using mechanical or chemical processes (Table 14.4). This method uses current lithographic methods used in microelectronics for producing integrated electronic circuits at nanoscale. Photolithography and lithography using electron beams are, in particular, two of the most widely used *top-down* techniques.

However, as one approaches sizes below 100 nm the resolution and replication speed of top-down approaches limit the efficiency, and consequently in this size regime the *bottom-up* ('from small to large') technology becomes important (Table 14.5).

Bottom-up techniques allow processing and manipulation at atomic scale and lead to nanomaterials and nanostructures. When atoms are regrouped, they form molecules with variable complexity, usually with a polyhedral shape (at the scale of Å). These structures have several hundred (or thousand) atoms, which mean that the nanoparticles can grow in size up to the order of micron. *Self-assembly* is one common *bottom-up* method in biological processes.

Of the many *bottom-up* techniques, the sol-gel process is one of the most promising. This method is based on colloidal chemistry, where solid nanoparticles

Table 14.4 *Top-down* approaches for devices fabrication

Nanostructures Fabricated by Top-Down Processes

Lithographic techniques

- **Photo**lithography
- Phase shifting **optical** lithography
- **Electron beam** lithography
- **X-ray** lithography
- **Focused ion beam** lithography
- **Neutral atomic beam** lithography

Soft lithography

- **Microcontact printing**
- **Molding**
- **Nanoimprint**
- **Dip-pen nanolithography**

Table 14.5 *Bottom-up* approaches for film deposition

➡ ***Film Deposition Methods***

bottom-up approaches

Vapor Deposition Methods

Physical Vapor Deposition (PVD)

- Vacuum **Evaporation** / Molecular Beam Epitaxy (**MBE**)
- **Sputtering**
- Pulsed Laser Deposition (**PLD**)

Chemical Vapor Deposition (CVD)

- Thermal activaction (thermal **CVD**)
- Photochemical (**PCVD**)
- Low pressure (**LPCVD**)
- Laser assited (**LACVD** or **LCVD**)
- Plasma assited (**PACVD**, **PECVD**)
- Metal organics (**MOCVD**)
- Chemical beam epithaxy (**CBE**)

Sol-Gel Processing

- **Spray** coating
- **Spin** coating
- **Dip** coating
- **Electroplating**
- **L**iquid **P**hase **E**pitaxy

(monomers) are hydrolyzed (Eq. (14.33)), giving rise to a colloidal suspension (sol); in a second stage, condensation (of the monomers) takes place (Eqs. (14.34) and (14.35)), forming a gel.

$$\text{M-(OR)}_n + {}_x\text{H}_2\text{O} \leftrightarrow \text{(OH)}_x\text{-M-(OR)}_{n-x} + {}_x\text{ROH} \tag{14.33}$$

$$\text{(OH)-M-(OR)}_{n-x} + \text{(OH)-M-(OR)}_{n-x} \rightarrow \text{(OR)}_{n-x}\text{-M-O-M-(OR)}_{n-x} + \text{H}_2\text{O} \tag{14.34}$$

$$\text{M(OR)}_n + \text{(OH)-M-(OR)}_{n-x} \rightarrow \text{(OR)}_{n-x}\text{-M-O-M-(OR)}_{n-x} + \text{ROH} \tag{14.35}$$

Although the *bottom-up* processes have been less developed than the *top-down* techniques, there are greater expectations about the *bottom-up* techniques.

14.3 Civil Engineering Nanomaterials: Case Studies

14.3.1 Traditional Construction Materials Whose Performance Is Increased by the Presence of Nanoparticles

14.3.1.1 Nanoparticles in Portland Cement

One of the desirable contributions of the cement production to sustainability includes composition reformulation, like the reduction of limestone or the partial substitution of cement by industrial subproducts (see Chap. 1). The improvement of cement technology includes the innovation of the productive process, namely by the presence of nanoadditives, capable of accelerating reaction steps or promoting innovative properties such as *self-healing*, for example.

In Portland cement, several raw materials have been tested in the form of nanoparticles. The reduction of the nanoparticles' size interferes in the cement's reaction kinetics—generally, the cure is faster and the cement harder. The presence of more intense electrostatic forces and the bigger superficial area is responsible for such behavior.

Resistance to flexion and compression is also enhanced in Portland cement by the presence of nanoparticles of silica (SiO_2), of hematite (Fe_2O_3), or of organically modified montmorillonite $[(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O]$.

In the case of hematite nanoparticles, the upgradation of the mechanical resistance of Portland cement is attributed to the increase in reactivity in the hydration reactions. The maximum addition is, however, of 10 % in weight, being the maximum of resistance obtained at a 3 % in addition weight [19].

The substitution of silica microparticles by silica nanoparticles was also investigated. The increase of silica reactivity (due to increase in surface area) allows for reductions to half of the silica contend in the cement composition and enhances the cement mechanical performance.

Nevertheless, the reduction of the working (temperature and/or viscosity) range, the cost of the final product along with the presence of a huge number of cracks (responsible for the cement' fracture under lower loads) are more than enough motives to dissuade the addition of silica nanoparticles to cement [19].

The inclusion of alumina nanoparticles raises the elasticity module of cement [20].

14.3.1.2 Nanoparticles in Pavement

The increase in the volume of traffic (particularly heavy vehicle traffic) and erosion (intensify by climate change) may raise the load on pavement. The absence of suitable maintenance/repair after long periods of service may decrease the estimated lifetime in many construction materials. The traditional pavement repair processes (based on the overlap of new layers) lead to an immediate relative improvement, yet follow by long-term deterioration, particularly on routes subject to high volume of traffic.

The incorporation of modified polymers in binder's formulation (to be used in pavements) was one of the earliest attempts to enhance pavement' load resistance. To improve the performance and durability of pavements, the addition of nanoparticles to bituminous binders stands up as a promising option. The presence of carbon nanoparticles in binders for asphalt, and their effect on the rheological properties with aging, is another current research topic [21].

The presence of nanoparticles or nanofibers increases the abrasion resistance in pavement. The abrasion resistance (which is a direct function of the compressive strength) increases with TiO_2 nanoparticles contend, followed by SiO_2, and only then with the presence of polypropylene (PP) nanofibers. For all of these embodiments, there is a maximum concentration value of nanoparticles/nanofibers, from which the effect on abrasion resistance decreases [22].

14.3.1.3 Hardened Metals with Nanodispersion

There are several mechanisms able to enhance the mechanical strength of metallic materials—hardening by solid solution, by precipitation, or by deformation is just the most common. All these mechanisms are well known and have been extensively studied. The innovation is focused on nanoparticles' effect on these mechanisms, how they are able to improve and to enhance the traditional materials' properties.

The hardness of copper (Cu) increases with Cu nanoparticles decreases. Copper nanoparticles of 5 nm exhibit a hardness of ~2,000 MPa, ten times higher than in coarse Cu [17]. The grain boundaries act as barriers to the dislocations slip—grain boundaries are located randomly and the slip plans in a grain are hardly coplanar with the slip plans in adjacent grain (see Chap. 9). The resistance of the obstacle (grain boundary) is measured by the applied force needed to slip cross a grain boundary and activate the slip in the adjacent grain. A grain boundary promotes the accumulation of dislocations, until being actuated by a force greater enough to allow dislocations to slip across them.

The smaller the size of the nanoparticle, the lower the number of dislocations that may queue in grain boundaries, but the higher the stress required for their propagation [17].

14.3.1.4 Coated Glasses

In glasses, the presence of nanoparticles can occur in two ways—on the surface (when incorporated in the glass coatings, *see* Chap. 8) or in bulk (when introduced during the glass melting). In either cases, the presence of nanoparticles can enhance or even introduce new optical, optoelectronic, photochromic or catalysis properties—the COATED GLASSES are an example (Anti-Reflection, MIRROR and LOW-Emissivity Glasses, *see* Chap. 8). The manufacture of COATED GLASSES is often protected by industrial secrecy.

14.3.2 Eco-Active Building Materials (Removing Pollution, Antibacterial, and Self-Cleaning Properties)

14.3.2.1 The Photocatalyst Effect

The photocatalyst role of titanium dioxide (TiO_2) is well known: when exposed to UV light, TiO_2 not only induces the catalyst process [20] in substances attached to their surface, but also induces hydrophilic self-conversion [23].

Its role as a catalyst means TiO_2 is not consumed during reaction processes. It is still extremely hydrophilic (contact angle is 0° or close to 0º) which means water (rainwater or washing water) forms a continuous film on its surfaces which contain titania (either as a TiO_2 film/coating or through the impregnation with TiO_2 nanoparticles), which stops drips forming and eases cleaning, for example, on the outside of buildings (*see* Sect. 14.2.3.2). It has also antibacterial properties (*Escherichia coli (E. coli), Klebsiella pneumoniae* and *Staphylococcus aureus*) and is recommended for internal or external use, wherever cleanliness and hygiene are paramount, such as in operating theatres, medical labs, hospitals, and restaurant/canteen kitchens.

By decomposing polluting agents, the reactions photocatalyzed by TiO_2 (either oxidation or reduction) occur at the surface of TiO_2 nanoparticles or at the surface of films/coatings containing TiO_2. The different forms of active oxygen produced—O_2^-, $^{\bullet}OH$, $HO^{\bullet}_2$ and $O^{\bullet}$—are responsible for breaking down polluting agents, either organic or inorganic.

$$e^- + O_2 \rightarrow O_2^-(\text{ad}) \tag{14.36}$$

$$O_2^-(\text{ad}) + H^+ \rightarrow HO_2^{\bullet}(\text{ad}) \tag{14.37}$$

$$h^+ + H_2O \rightarrow {}^{\bullet}OH(\text{ad}) + H^+ \tag{14.38}$$

$$h^+ + O_2^-(\text{ad}) \rightarrow 2^{\bullet}O(\text{ad}) \tag{14.39}$$

Its high photocatalytic efficiency, thermodynamic stability, and low cost make titanium dioxide (TiO_2) the prime candidate for photocatalyst uses at an industrial scale. To ease/increase photocatalyst yields, TiO_2 nanoparticles are impregnated either in the mass or at the surface. The main applications are the photocatalytic decomposition of pollutants, self-cleaning or anti-condensation functions, visible reaction to radiation, hydrophilic/hydrophobic properties, and even the treatment of contaminated soils or waste water.

The presence of TiO_2 in pavements allows nitrogen dioxide (NO_2) to be converted into nitrates, reducing urban pollution levels [23]. The photocatalytic properties of TiO_2 are, however, dependent on the intensity of sunlight (UV levels) and the number of hours of light exposure (both of which are dependent on geographical position and season). For inside use, exposure to artificial sources of UV light is governed by specific safety regulations.

14.3.2.2 Self-Cleaning Mortars

The PICADA project (Photocatalytic Innovative Coverings Applications for Depollution Assessment) programme was developed as part of the Competitive and Sustainable Growth EU programme. The project carried out laboratory and real scale experiments to assess the benefits of the presence of titanium dioxide (TiO_2) in building materials and surfaces. The project's aims included studying the mechanisms of photocatalytic reactions, their self-cleaning and pollution-reducing qualities, developing and optimizing industrial formulations containing TiO_2, application methods, establishing a behavior model in real urban environments, and even developing and marketing products.

Several building materials were tested in the PICADA project, including: a synthetic mortar for decorative topcoat, based on white Portland cement with a titanium content of 3 % wt, developed and sold by ITALCEMENTI Co; cement-based mortars with titanium (0.5, 1.3, and 6 % wt TiO_2, in an anatase/rutile ratio of 80/20 % wt) nanoparticles (particles ~ 21 nm in diameter); an aqueous coating for glass, containing 5–10 % wt titanium, to be applied during building work; a white acrylic paint with 10 % wt TiO_2.

The Italian cement manufacturer ITALCEMENTI has patented products developed in the PICADA project and has produced a range of products which contain titanium dioxide, branded TX Active. A reduction in nitrogen oxide levels around 60 % wt was registered in a central street in Milan with pavements made with products in the TX Active range, and a reduction of 45 % wt in industrial areas. ITALCEMENTI estimates a reduction of 50 % in nitrogen oxides in cities in which only 15 % of exterior surfaces (paint on buildings, streets, etc.) used TX Active products.

In Rome, the Church *Dives in Misericordia* was built using cements from the TX Active range [22].

14.3.2.3 Self-Cleaning Glass

As part of the Sixth Framework Programme for Research and Technological Development 2004, a project was carried out on Self-Cleaning Glass, whose objectives focused on developing scientific knowledge on glass reactions in highly polluted environments, the mechanisms and design of self-cleaning functions for glass, developing methods to measure dirt levels, developing European regulations on self-cleaning glass, and acquiring fundamental knowledge on self-cleaning glass.

Today there are several different self-cleaning glasses on the market, such as Radiance Ti^{TM} (AFG Industries), LO-E2 Plus^{TM} (Cardinal IG), DIAMOND GUARD^{TM} (Guardian Ind.), ACTIV^{TM} (Pilkington), SUN CLEAN^{TM} (PPG Industries), and AQUACLEAN (Saint Gobain).

14.3.2.4 Ceramic Surfaces with Self-Cleaning Qualities

Ceramics whose glaze includes titanium dioxide are anti-bacterial, in addition to being self-cleaning, making them the best choice for settings where hygiene and sterilization are paramount. There are several products on the market, such as ACTIVE (Active Clean, Australia), Strata Tiles (United Kingdom), Toto's Hydrotect (Japan).

14.3.2.5 Self-Cleaning Steel

In steel, as well as the anti-bacterial properties observed in other matrices, the decomposition of stearic acid when TiO_2 was present was also observed. GE CleanSteel, Bosch, and AMANA are some of the companies which sell steel with self-cleaning properties.

14.3.2.6 Aqueous Coatings with Self-Cleaning Qualities

As well as the products already mentioned (which include self-cleaning functions), there is a liquid product on the market with self-cleaning, anti-bacterial and tuneable hydrophilic/hydrophobic character which can be applied through spraying to any surface. Some of the products already on sale are Nansulte (Industrial Nanotech Inc.), TiPE^{TM} Nano Coat (Advanced Nano Technology), and EnviroCare TiO_2 Photo-Compound Range (Altimate EnviroCare). Spraying these products on the outside of buildings, streets, and pavements gives their surfaces:

1. protection against dust (by reducing electrostatic uptake)
2. protection against acid rain (by hydrophobic character) and atmospheric pollutants (by possible chemical decomposition)
3. stopping the growth of fungi/bacteria/algae on surfaces (by interfering in microorganisms' metabolisms)
4. decomposition of organic waste (through different forms of active oxygen groups)
5. slowing down aging of surfaces, by absorbing the UV rays in sunlight

14.3.3 Building Materials with Self-Healing Properties

14.3.3.1 Self-Healing Methods

Mimicking biological processes has led to self-healing in engineering. Self-healing is the ability to repair and reinstate original material properties, after thermal, mechanic, ballistic, or other types of deterioration. The ability to self-healing is

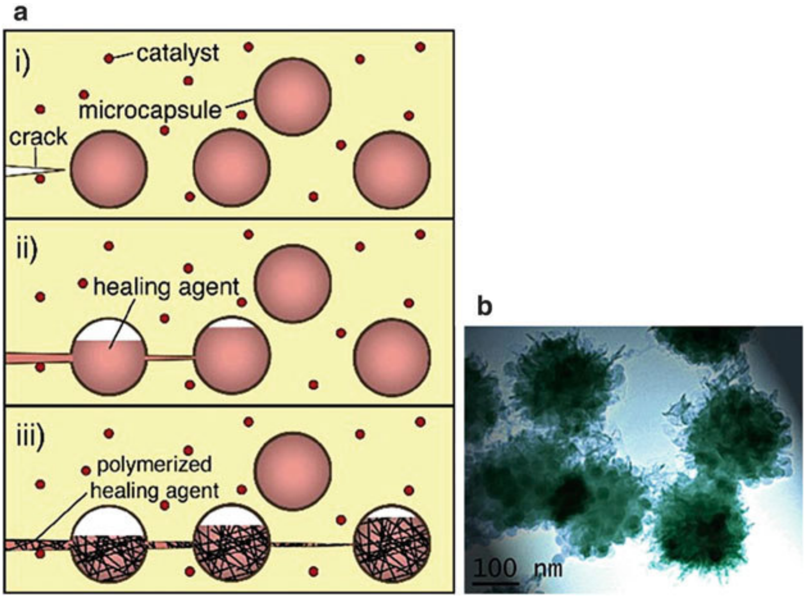


Fig. 14.42 Self-healing mechanism: (**a**) sketch and (**b**) SEM photography of a polymeric self-healing product inside a matrix. Image Credits: https://www.google.pt/search?q=selfrepair+polymeric+building+materials&source

incorporated in polymer, metallic, ceramic, or composite materials. Depending on the type of material and the cause of deterioration, several self-healing mechanisms have been proposed [24].

One of the most recent methods is the concept of autonomous self-healing [25, 26]. A self-healing agent is microencapsulated (and not nanoencapsulated) and introduced into an epoxy matrix (for composites with a *polymer matrix*). The composite matrix contains the catalyst for polymerisation of the self-healing fluid. After the first cracks form, through material deterioration, for example, the microcapsules in the matrix break and release the self-healing agent, which fills in the cracks through capillary action. As soon as the self-healing agent comes into contact with the catalyst (dispersed throughout the matrix), polymerisation reactions begin, which will lead to the healing of the nano- or micro-cracked surface and recovery of the material's original properties (Fig. 14.42).

14.3.3.2 Self-Healing Cement

The self-healing cement is directed to applications where the resistance to radiation is crucial, as reservoirs of flammable products or waste storage. The self-healing cement reduces the maintenance costs in the medium and long term, as well as the costs associated with maintenance and repairs [27, 28].

14.3.4 Building Materials with Antibacterial Properties

14.3.4.1 Antibacterial Ceramic

Antibacterial ceramic has application in hospitals, kitchens, and anywhere that requires an environment free of germs or bacteria. An *antibacterial* ceramic, capable of inhibiting microbial growth, contributes to a healthier environment. An *antibacterial* ceramic is one of the examples of nanotechnology in ceramics. The *antibacterial* ceramic is coated with a glaze, to which were added 200–400 ppm of silver nanoparticles (Ag^0), with 1–10 nm radius. Silver nanoparticles exhibit a high antibacterial/antifungal spectrum (>650 kinds of bacteria and yeast) even at very low concentrations. The metallic or ionic silver nanoparticles cross the cell walls (cell membrane) of bacteria and other microorganisms, impairing them (i.e., making them unable to function, grow, or reproduce) [29].

TiO_2 is another common antibacterial agent (as discussed in Sect. 14.3.2).

14.3.4.2 Antibacterial Paints and Coatings

The presence of nanoparticles in paints and coatings can enhance the brightness and/or color and introduce new properties in the material, such as antibacterial and self-cleaning ones, or even the decomposition of pollutants. The color will vary in response to *stimuli*, such as temperature or chemical environment, or, for example, limit the absorption of light in the infrared range, contributing to the reduction of energy losses of the building.

Antifouling paints can benefit from nanoadditives, given the ecological impact of tributyl tin.

The photocatalytic role of titanium oxide (TiO_2) or the antibacterial role of silver (Ag^0) allows its use in antibacterial paints.

The incorporation of nanoparticles in paint and coatings allows reducing the number or thickness of layers (of paint or coating) to be applied, a reduction in the final body-weight of the object, and also a decrease in the volume of solvents used in the process, which, in the environmental sustainability, is recommended [30].

14.3.5 Building Materials with Photovoltaic Properties

Solar energy results from the conversion of solar energy into electricity, directly by the photoelectric effect. Solar energy is a renewable energy classified as clean energy or green energy. However, although this type of energy does not produce pollution or environmental impacts, the reuse or recycling of photovoltaic cells, at the end of the life cycle, is not yet implemented. According to Greenpeace, the photovoltaic power could ensure the needs of two thirds of the world population in 2030.

One of the great advantages of solar energy is that the unit cost of power produced is independent of the scale of production. For this reason, the integration of photovoltaic cells in buildings has aroused enormous interest.

The integration of technology at the nanoscale in photovoltaic cells is still under investigation, and one believes that it will increase the low efficiency of such devices while lowering costs. Among various research projects one highlights the incorporation of titanium dioxide nanotubes, quantum dots of lead selenide, or carbon nanotubes/bucky-balls [31].

14.4 Nanotechnology and Toxicity

Man has always been exposed to nanometric particles (<100 nm); however, in recent decades human activities have increased this exposure enormously. High levels of industrialization and, in particular, nanotechnology, have increased inhalation, ingestion, skin exposure, and injection of nanomaterials in humans.

When inhaled, nanoparticles can remain in the respiratory system. Their size allows them to enter cells and/or epithelium and endothelium cells through transcytosis, and can reach the circulatory and/or lymphatic system, and ease deposition on potentially sensitive targets, such as in bone marrow, lymphatic nodes, or the heart. Nanoparticles have already been observed in the central nervous system and ganglions. In some cases, nanoparticles could have moved from the skin and reached the lymphatic channels.

Nanoparticles' large surface area, relative to microparticles with the same chemical composition, makes them more active from a physiological point of view. This activity includes potential inflammatory and pro-oxidant substances, which explains the high toxicity of nanoparticles for several biological species.

In 2006, the Royal Commission on Environmental Pollution raised the first alert on the possibility of damage in humans caused by nanoparticles. In fact, biological defence systems are not ready to fight foreign bodies measuring only a few nanometres [32]. In 2008, the first new story appeared in the press confirming a link between poisoning and nanoparticles in a type of paint (in China). Some citizen groups have called attention to the non-explicit use of nanoparticles in products such as cosmetics.

Conclusions

Nanotechnology is an incredibly broad and interdisciplinary field, requiring integrated skills in Physics, Chemistry, Materials Science, Biology, Mechanical and Electronic Engineering and, sometimes, even Medicine. Nanotechnology gives us new and extraordinary opportunities to manufacture and understand new materials and devices in all fields of science and engineering.

The civil engineering productive sector is traditionally conservative and fragmented, being mainly comprised by small- and medium-sized companies. This is one of the main factors why investigation and development of nanoproducts in civil engineering is still in its beginnings, when compared with pharmaceutical and medicinal sectors. Notwithstanding the youth of nanotechnology in Civil Engineering, it is a promise growing area of scientific and economical interest. Today several examples of nanomaterials and nanodevices hit the civil engineering market, and many more are under investigation and development.

Introduction to Nanomaterials

- Ashby MF, Ferreira PJ, Schodek DL (2009) Nanomaterials, nanotechnologies and design. An introduction for engineers and architects. Elsevier. ISBN 978-0-7506-8149-0
- Cao G (2007) Nanostructures & nanomaterials. Synthesis, properties & applications. Imperial College, London. ISBN 1-86094-480-9
- Wautelet M et coll (2003) Les nanotechnologies. Dunod. ISBN 2 10 007954 9
- Rubahn H-G (2008) Basics of nanotechnology. Wiley. ISBN 978-3-527-40800-9
- Goddard M III, Brenner DW, Lyshevski SE, Iafrate GJ (eds) Handbook of nanoscience, engineering and technology. CRC. ISBN 0-8493-1200-0

Nanotoxicology

- Suh WH, Suslick KS, Stucky GD, Suh Y-H (2009) Nanotechnology, nanotoxicology and neuroscience. Prog Neurobiol 87:133–170
- Oberdörster G, Oberdörster E, Oberdörster J (2005) Nanotoxicology: an emerging discipline evolving from studies of ultrafine particles. Environ Health Perspect 13:823–839

Scientific Publications

- *Nature Nanotechnology*
- *Nanotechnology*
- *Nanotechnology Journal*
- *Journal of Nanoscience and Nanotechnology*
- *Journal of Nanotechnology—An Open Access Journal*

Products and Supliers

- http://www.nanovip.com
- http://www.nanoindustries.com
- http://nanotechnology.com
- http://nanotech-now.com
- http://www.investorideas.com
- http://jazdtech.com/techdirect/cat/Emerging-Technology/Nanotechnology.htm

Societies and Organizations

- http://www.understandingnano.com
- http://www.nanotech-now.com
- http://www.nano.gov
- http://crnano.org
- http://sciencedaily.com
- http://www.discovernano.northwestern.edu

References

1. Feynman RP (1960) There's plenty of room at the bottom. Eng Sci 23:22–36, http://www.zyvex.com/nanotech/feynman.html
2. Taniguchi N (1974) Proceedings of the international conference on production engineering, Tokyo Part II, Japan Society of Precision Engineering
3. Drexler KE (1981) Molecular engineering: an approach to the development of general capabilities for molecular manipulation. Proc Natl Acad Sci U S A 79:5275–5278
4. Moore GE (1965) Electronics 38(8):114–117
5. Gonçalves MC, Martins B (2014) Multifunctional core-shell nanostructures. In: Ali N, Seifalian A (eds) Nanomedicine. One Central Press Office, Manchester (ISBN 978-1-910086-00-1 Hardback; 978-1-910086-01-8 eBook-PDF)
6. Yablonovitch E (1987) Inhibited spontaneous emission in solid-state physics and electronics. Phys Rev Lett 58:2059–2062
7. John S (1987) Strong localization of photons in certain disordered dielectric superlattices. Phys Rev Lett 58:2486
8. Iijima S (1991) Nature 354:56
9. Siegel RW (1994) J Phys Chem Solids 55:1097
10. Gonçalves MC, Attard GS (2003) Nanostructured mesoporous silica films. In: Gogotsi YG, Uvarova IV (eds) Nanostructured materials and coatings for biomedical and sensor applications, vol 102, NATO science series, II. Mathematics, physics and chemistry. Kluwer Academic, Dordrecht, pp 159–168. ISBN 1-4020-1321-3
11. Hugh Tait (ed) (1999) Five thousand years of glass. Published for the Trustees of the British Museum, by British Museum Press, London
12. Ashby MF, Ferreira PJ, Schodek DL (2009) Nanomaterials, nanotechnologies and design. An introduction for engineers and architects. Elsevier, New York
13. Gonçalves MC, Almeida RM, Braz J (2007) Process optimization of sol-gel derived colloidal photonic crystals. J Sol-Gel Sci Technol 42:135–143
14. Almeida RM, Gonçalves MC (2006) Sol-gel derived photonic bandgap structures. In: Balda R, Pandalai SG (eds) Photonic glasses, pp 1–22. ISBN 81-308-0063-2
15. GAMGI, General Atomistic Modelling Graphic Interface. http://www.gamgi.org
16. Wautelet M et coll (2003) Les nanotechnologies. Dunod, Paris
17. Cao G (2007) Nanostructures & nanomaterials. Synthesis, properties & applications. Imperial College, London
18. Porter DA, Easterling KE (1992) Phase transformations in metals and alloys. Chapman & Hall, London
19. Meyers MA, Lin AY, Chen P, Muyco J (2008) J Mech Behav Biomed Mater 1:76–85
20. Fujishima A, Zhang X, Tryk DA (2008) Surf Sci Rep 63(12):515–582
21. http://www.bast.de/nn_74576/EN/E-Forschungsprojekte/e-laufende/e-fp-laufend-s3.html
22. http://italcementigroup.com/ENG/Media+and+Communication/News/building+and+Architecture/20031126.htm

23. Hashimoto K, Irie H, Fujishima A (2005) Jpn J Appl Phys 44(12):8269–8285
24. Wool RP (2008) Soft Matter 4:400–418
25. Sottos N, White S, Bond I (2007) J R Soc Interface 4:347–348
26. Blaiszik BJ, Sottos NR, White SR (2008) Compos Sci Technol 68:978–986
27. Coatings via self-assembly of smart nanoparticles (Chapter 7, pp 145–157). In: Minko S, Luzinov I, Motornov M, Sheparovych R, Lupitskyy R, Liu Y, Klep V (eds) Smart coatings II. ACS symposium series, vol 1002. American Chemical Society, Washington, DC. doi:10.1021/bk-2009-1002.ch007, ISBN13: 9780841272187, eISBN: 9780841272194, Publication Date (Print): 27 Mar 2009
28. Wu DY, Meure S, Solomon D Self-healing polymeric materials: a review of recent developments. www.elsevier.com/locate/ppolysci
29. Whitesides GM, Grzybowski B (2002) Self-assembly at all scales. Science 295:2418–2421
30. Beck JS, Vartuli JC, Roth WJ, Leonowicz ME, Kresge CT, Schmitt KD, Chu CT-W, Olson DH, Sheppard EW, McCullen SB, Higins JB, Schlenker JL (1992) J Am Chem Soc 114:10834
31. Kresge CT, Leonowicz ME, Roth WJ, Vartuli JC, Beck JS (1992) Nature 359:710
32. Suh WH, Suslick KS, Stucky GD, Suh Y-H (2009) Nanotechnology, nanotoxicology and neuroscience. Prog Neurobiol 87:133–170

Corrosion

15

João Salvador Fernandes and Fátima Montemor

Abstract

This chapter aims at providing a tool for understanding the most important issues related to corrosion-induced degradation and the most suitable strategies for reducing the impact of corrosion, preserving the material integrity.

It overviews the most important concepts related to corrosion and its impact on material life cycle, being organised in five subchapters dealing respectively with the definition and impact of corrosion, the electrochemical principles governing the corrosion processes, the classification of the most important corrosion types, the need for proper selection and design of materials and the main strategies and technologies for corrosion protection. Finally, it addresses how the performance of reinforced concrete structures is affected by corrosion processes occurring at the rebars.

Keywords

Cathodic protection • Biological corrosion • Crevice corrosion • Corrosion of polymers • Corrosion of stone materials • Environmentally induced cracking • Filiform corrosion • Galvanic corrosion • Intergranular corrosion • Pitting corrosion • Selective leaching • Uniform corrosion • Corrosion inhibitor • Corrosion potential • Electrochemical series • E-pH (Pourbaix) diagram • Galvanic series • Immunity • Passivity • Weld decay

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M.C. Gonçalves, F. Margarido (eds.), *Materials for Construction and Civil Engineering*, DOI 10.1007/978-3-319-08236-3_15

15.1 Introduction

15.1.1 Definition of Corrosion

Corrosion can be defined as deterioration of a material through the action of the surrounding environment, alone, or in conjunction with mechanical forces. For metals, corrosion generally involves oxidation, and is therefore an electrochemical phenomenon. However, the definition of corrosion includes other cases—such as the deterioration of stone, wood, or plastic—that do not involve electrochemical processes.[1]

Metallic corrosion is a consequence of the material's tendency to evolve into its state of least energy. To produce a metal from its ore, that is, from the form that occurs naturally, energy must be given. During its life cycle, metal will tend to oxidize, reverting to its primitive state. The greater the amount of energy required to produce a metal, the greater its tendency to corrode. This energy varies from metal to metal, being very high for metals like magnesium and very low for metals like silver and copper (gold occurs naturally in the metallic form and does not tend to corrode). In Table 15.1, some common metals are presented, ordered according to energy required to produce them and, therefore, according to their tendency to corrode.

15.1.2 Importance and Costs of Corrosion

Corrosion can cause significant damage to practically all materials, from electrical appliances or cars to large water or gas supply systems and other structures, ships, etc.

The direct costs of corrosion include the costs of corrosion management (inspection, maintenance, repair, and rehabilitation, covering the cost of replaced parts as well as energy and labor force needed to carry out the replacement), the costs of the creation, and maintenance of protection systems (coatings, cathodic protection, etc.) and those caused by loss of productive time at industrial plants (for cleaning, repairs, or replacement of corroded components), loss or contamination of products, or loss of efficiency (e.g., heat transfer in heat exchangers). The indirect costs of

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[1] DIN EN ISO 8044 standard defines corrosion as "physical interaction between a metal and its environment which results in changes of the metal's properties and which may lead to significant functional impairment of the metal, the environment or the technical system of which they form a part," making it clear that corrosion applies to metals. IUPAC defines corrosion as "an irreversible interfacial reaction of a material (metal, ceramic, polymer) with its environment which results in consumption of the material or in dissolution into the material of a component of the environment," widening the concept to any other material.

Table 15.1 Order of some metals according to energy needed to produce them

Less energy needed for production	Gold	Lower tendency to corrode
↕	Platinum	↕
	Silver	
	Copper	
	Lead	
	Tin	
	Nickel	
	Iron	
	Chromium	
	Zinc	
	Aluminum	
More energy needed for production	Magnesium	Greater tendency to corrode

corrosion are incurred by others than just the owners or operators of the structure, being harder to quantify, such as those related to the safety of the facilities, where failures can lead to human losses (cars, airplanes, bridges, piping, tanks, etc.), interruptions in communications (corrosion of buried telephone cables), traffic delays (e.g., repair of a bridge), or the loss of artistic heritage (degradation of monuments).

In a recent study carried out in the USA [1], it was concluded that the annual costs due to corrosion in the country reached 276 billion dollars in 1998, that is, 3.1 % of its gross national product (by comparison, the annual cost to the USA of natural disasters, such as hurricanes, floods, droughts, and fires, was 17 billion dollars).

15.2 Corrosion Basics

Practically all metallic corrosion processes involve charge transfer in an aqueous medium. Therefore, before describing the different forms of corrosion, the basics of the electrochemical processes involved in corrosion will be briefly discussed.

15.2.1 Electrochemical Reactions

Let us consider the corrosion reaction for zinc in acidic medium, represented by the following overall reaction:

$$Zn + 2H^+ \rightarrow Zn^{2+} + H_2 \tag{15.1}$$

This reaction can be divided into two processes, one involving zinc and the other involving the H^+ ions of the acidic solution:

$$Zn \rightarrow Zn^{2+} + 2e^- \tag{15.2}$$

$$2H^+ + 2e^- \rightarrow H_2 \tag{15.3}$$

The first equation corresponds to the zinc oxidation reaction, while the second represents the reduction reaction for the H^+ ions, with formation of gaseous molecular hydrogen.

An *oxidation* reaction is characterized by a loss of electrons or an increase in the oxidation number of a given species (in this case, zinc), which is generally equivalent. The electrode where oxidation occurs is called the *anode*, and therefore oxidation can also be called the *anodic reaction*. On the other hand, a *reduction* reaction is characterized by the transfer of one or more electrons to a certain chemical species, its oxidation number decreasing. The electrode where reduction occurs is called the *cathode*, and therefore reduction can also be called the *cathodic reaction*.

An electrochemical reaction can therefore be broken down into four partial processes: an anodic reaction, consisting in oxidation of the metal, producing ions that pass into the corrosive environment and electrons in the metal; the transportation of electrons through an electrical conductor (metal) from the anode to the cathode; the transportation of ions through an ionic conductor (corrosive environment); a cathodic reaction, representing the reduction of species in solution (in the corrosive environment) at the expense of the electrons that have arrived at the cathode in the meantime, generally producing gases or metal deposits (Fig. 15.1).

Anodic reactions involved in metal corrosion are invariably of the $Me \rightarrow Me^{n+} + ne^-$ type, as in silver oxidation ($Ag \rightarrow Ag^+ + e^-$), iron oxidation ($Fe \rightarrow Fe^{2+} + 2e^-$), or aluminum oxidation ($Al \rightarrow Al^{3+} + 3e^-$). Cathodic reactions relevant to corrosion are not so many. The simplest and most common reaction is the reduction of H^+ ions to gaseous hydrogen in an acidic medium. The reduction of dissolved molecular oxygen is also common when working in environments exposed to the air, and can be represented by the following equations, for neutral and alkaline media and in acidic media, respectively:

$$O_2 + H_2O + 4e^- \rightarrow 4OH^- \tag{15.4}$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \tag{15.5}$$

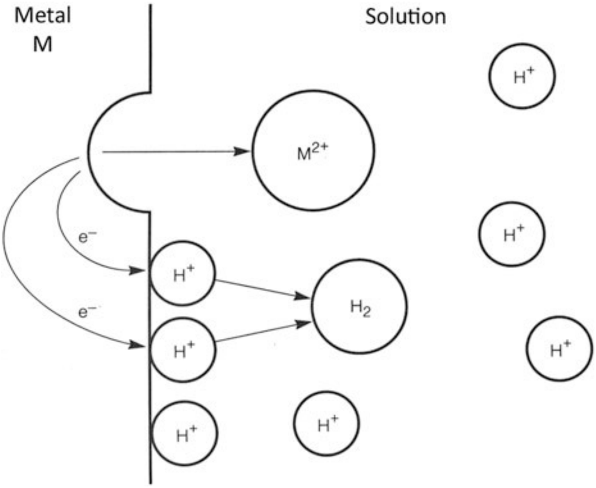


Fig. 15.1 An outline of the processes involved in the electrochemical corrosion of metals (adapted from [2])

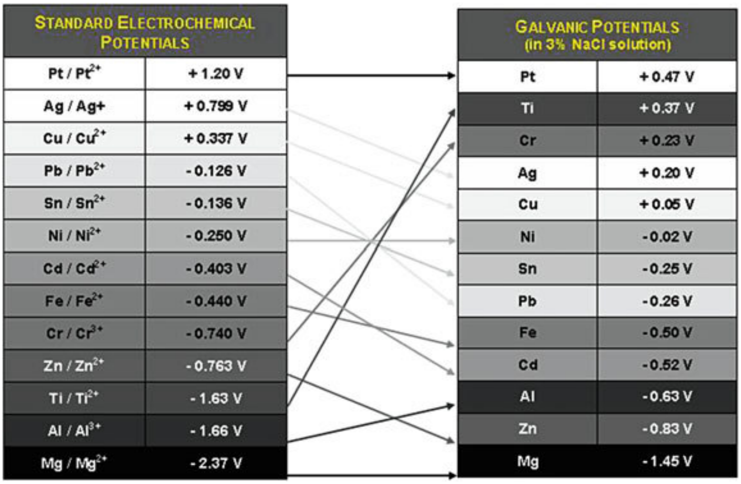
In the presence of oxidized species in solution, they can also be reduced on the surface of the metal, promoting corrosion. This is the case of iron corrosion in solutions with copper ions, in which the electrons produced by the iron oxidation are consumed by the Cu^{2+} reduction reaction, with deposition of metallic copper on iron:

$$\mathrm{Fe} \rightarrow \mathrm{Fe}^{2+} + 2e^- \tag{15.6}$$

$$\mathrm{Cu}^{2+} + 2e^- \rightarrow \mathrm{Cu} \tag{15.7}$$

Based on the analysis of this last example, we could question what the criterion is that defines, in a bimetallic pair such as Fe/Cu, which metal has a greater tendency to oxidize, i.e., undergo corrosion. The answer to this question can be found in the thermodynamics of the reactions involved and, in particular, the different tendencies of metals to oxidize or reduce, which can be expressed by defining *reduction potential*. The greater the reduction potential of a certain metal electrode, the greater will be its tendency to reduce and, similarly, the lower its tendency to oxidize. The electrochemical series is commonly used to sort the different metals in terms of their nobility. The different equilibria are positioned depending on their respective standard electrode potentials (measured under standard conditions, that is, for a temperature of 25 °C and a unitary activity of ions in solution). By convention, a value of zero is assigned to the standard hydrogen electrode ($p\mathrm{H}_2 = 1$ atm, $a_{\mathrm{H}+} = 1$ g-ion L^{-1}, $T = 25$ °C), and the potentials of other systems are mentioned in relation to this electrode (SHE). An example on an electrochemical series is given in Fig. 15.2.

The conditions under which the standard potential is measured are rarely found in real systems, for several reasons: non-unitary activities of ionic species, temperatures other than 25 °C, the presence of impurities in the metal, formation



STANDARD ELECTROCHEMICAL POTENTIALS	
Pt / Pt^{2+}	+ 1.20 V
Ag / Ag+	+ 0.799 V
Cu / Cu^{2+}	+ 0.337 V
Pb / Pb^{2+}	- 0.126 V
Sn / Sn^{2+}	- 0.136 V
Ni / Ni^{2+}	- 0.250 V
Cd / Cd^{2+}	- 0.403 V
Fe / Fe^{2+}	- 0.440 V
Cr / Cr^{3+}	- 0.740 V
Zn / Zn^{2+}	- 0.763 V
Ti / Ti^{2+}	- 1.63 V
Al / Al^{3+}	- 1.66 V
Mg / Mg^{2+}	- 2.37 V

GALVANIC POTENTIALS (in 3% NaCl solution)	
Pt	+ 0.47 V
Ti	+ 0.37 V
Cr	+ 0.23 V
Ag	+ 0.20 V
Cu	+ 0.05 V
Ni	- 0.02 V
Sn	- 0.25 V
Pb	- 0.26 V
Fe	- 0.50 V
Cd	- 0.52 V
Al	- 0.63 V
Zn	- 0.83 V
Mg	- 1.45 V

Fig. 15.2 Electrochemical series and galvanic series in 3 % NaCl solution

of an oxide layer on the surface of the metal, etc. Therefore, in Corrosion it is common to obtain tables of potentials in specific environments, known as galvanic series. Galvanic potentials are different from standard potentials, and the relative positions of the metals in the series may be reversed, as seen in Fig. 15.2.

From the analysis of the electrode potential of a given metal, the risk of the metal undergoing corrosion in a specific environment can be assessed. In fact, a metal only corrodes (anodic dissolution) if a simultaneous cathodic process exists with a potential higher than that of the metal electrode, which can consume the electrons produced in the metal oxidation. For example, in pure water, without oxygen, only metals with a potential lower than the hydrogen electrode potential may corrode.

15.2.2 Anodes and Cathodes in Corrosion Cells

The problem of determining the location of the anode and cathode in a corrosion cell now arises. If the cell is composed of two metals, the metal showing lower potential works as the anode and the metal with higher potential as the cathode, the reduction involving that metal or only species in the solution, as in the reduction of H^+ or dissolved oxygen. This happens, for example, when a copper bar and a zinc bar are connected and immersed in an acidic solution: the zinc works as the anode, being corroded, while only the reduction of H^+ occurs on the surface of the copper bar, releasing gaseous hydrogen.

If there is only one metal, corrosion may be caused by the presence of heterogeneities (grain boundaries, impurities, different phases of a metallic alloy, etc.) which lead to the formation of areas with slightly different potentials. In this case, in accordance with the *local cell theory*, the less noble areas work as anodes and the nobler areas will support cathodic processes. However, when this occurs, the effects of corrosion are located in the anodic areas, resulting in localized attack on specific areas of the metal, which is not always the case. To explain the occurrence of corrosion processes whose effects are uniformly distributed over the entire surface, the *mixed potential theory* predicts the existence of infinitely small anodes and cathodes, randomly distributed over the metal surface and exchanging positions over time. Therefore, one point that now works as an anode can behave as a cathode immediately afterwards, leading to a uniform corrosion attack.

15.2.3 Passivity

Metals like iron, nickel, chromium, cobalt, titanium, or aluminum, as well as some of their alloys, can undergo a loss of reactivity in certain environments and in conditions under which one would normally expect corrosion. This phenomenon, known as *passivation*, is the result of the formation of a solid protective layer, generally consisting of oxides and/or hydroxides, on the surface of the metal. This passive film will then act as a physical barrier between the environment and the metal, protecting it. In fact, passivation does not involve complete suppression of the corrosion reaction, but rather lowers its rate to levels that are normally 10^3–10^6 times smaller.

Depending on the potential of the metal or alloy in a certain environment, it may be passive or undergo corrosion. Above a critical potential (passivation potential, E_{p}) the metal is passive; below the E_{p}, the metal undergoes corrosion.

Passivation can be achieved by applying an electrical current, which increases the material's potential, or can be achieved spontaneously in certain metals. This is true for aluminum, chromium, zirconium, and also for stainless steels, obtained by adding chromium to steel. Therefore, stainless steels owe their corrosion resistance to the spontaneous formation of a passive film.

Quoting Macdonald [3], the passivity of metals and alloys is the single most important phenomenon responsible for our metals-based civilization. We all accept metals technology in our everyday lives, but few of us realize that most structural metals are viable in an engineering sense only because of the existence of a surface oxide film whose thickness may not exceed a few nanometers (several tens of atomic diameters). These films frequently isolate phases that, without kinetic restrictions, ordinarily react violently. Consider, for example, one of our most common structural metals, aluminum. This metal has a heat and a free energy of reaction with oxygen that are not too different from those for gasoline, yet every day we fly through the air in vehicles made from the former but powered by the latter. The continued structural integrity of the aircraft is due entirely to the aluminum oxide film that exists on the surface. Extensive rupture of this film over large areas of the surface can lead to catastrophic reaction of the underlying metal with the environment. For example, powdered aluminum is added to solid rocket fuels to boost the energy density of the propellant. Likewise, the aluminum superstructure of the frigate HMS Sheffield burned during the Falkland-Malvinas Island war after being struck by an anti-ship missile. In both cases, factors existed that rendered the oxide film on the surface mechanically and structurally unstable, resulting in the continued exposure of the underlying metal to oxygen at highly elevated temperatures.

Although the phenomenon of passivity has been known for more than 150 years, during which time numerous theories have been proposed to explain it, a satisfactory description of the passive state still eludes us. This state of affairs is due, in part, to the experimental difficulties in probing surface films whose thickness may not exceed a few nanometers, and also is due to the conceptual difficulty in using bulk phase concepts in formulating theoretical descriptions.

On the other hand, the protection provided to metals through passivity is not free from dangers, since some of the most dangerous forms of corrosion are those related to localized attack and rupture of the passive film.

15.2.4 Thermodynamic Stability and Potential-pH Diagrams

The behavior of a metal in a certain environment can fit into one of three domains: immunity, corrosion, or passivation.

A metal is said to lie in the *immunity* domain when the thermodynamically stable form is the metal itself. Therefore, the potential of an immune metal is lower than the oxidation reaction equilibrium potential, which means it does not undergo corrosion.

On the other hand, the *activity* (*dissolution* or *corrosion*) domains correspond to conditions where the stable forms are simple or complex ions of the metal. In this case, the potential should be above the oxidation reaction equilibrium potential, so the metal shows a tendency to corrode.

Passivity is the state in which the metal practically does not undergo corrosion, since its oxidation leads to the formation of solid products, as oxides or hydroxides. The potential of a passive metal is higher than that for the immunity domain. It should be noted that a passive metal can still corrode, although very slowly (passive corrosion). Moreover, oxide or hydroxide formation does not necessarily imply passivation, as passivation films must have adequate protective properties and must not tend to flake off or crack.

The immunity, activity, and passivation domains of a given metal are normally represented in the form of E-pH diagrams, also known as Pourbaix diagrams in honor of the Belgian scientist who spread their use [4]. Figure 15.3 shows the theoretical E-pH diagram for iron in an aqueous medium (left) and a simplified diagram showing the immunity, corrosion, and passivation domains (right). It is worth to note that E-pH diagrams are normally the result of theoretical calculations based on thermodynamic data, so they can only answer to the question on whether a particular corrosion process is thermodynamically viable or not. In fact, the extent of a corrosion process is also very much dependent on the reactions kinetics, which are not taken into account in the diagrams. Thus, it may happen that, although the

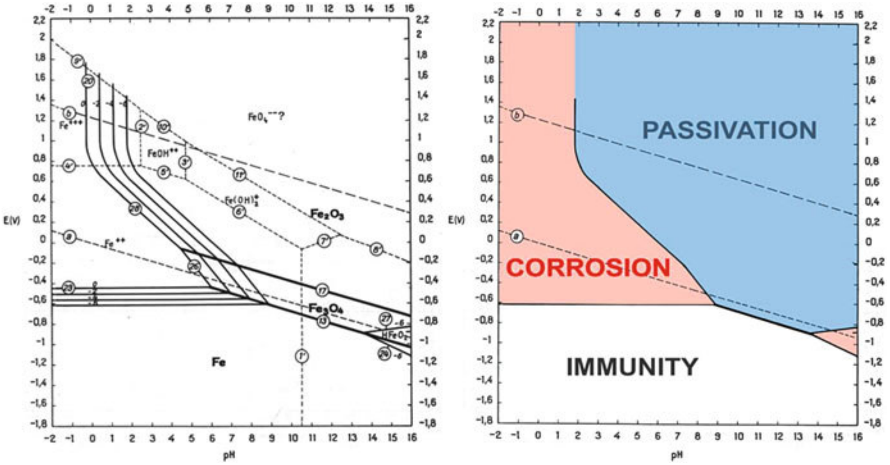


Fig. 15.3 Theoretical E-pH diagram for iron in aqueous media (*left*) [4] and respective simplified diagram showing the immunity, corrosion, and passivation domains (*right*)

E-pH conditions correspond to the corrosion or activity domain, the corrosion rate is so slow that the metal may be regarded as immune.

15.3 Types of Corrosion

Corrosion can occur in many forms, so correctly identifying the type is fundamental to assessing the phenomenon, i.e., to establishing the mechanism and applying appropriate protection measures. Each type of corrosion has particular characteristics, which are described in the following points. Figure 15.4 shows a brief summary of the different forms of corrosion.

15.3.1 Uniform Corrosion

Uniform or general corrosion is a type of corrosion that occurs evenly across the surface of a metal. The loss of material is more or less uniform in a given element of area, and the metal may lose its gloss and become rough—Fig. 15.5. For uniform corrosion to take place, the surface of the metal must be uniform in terms of its composition and metallurgy, and the corrosive medium must have equal access to all areas of the metal's surface. These conditions are rarely found in practice, so the definition of uniform corrosion has some tolerance for small heterogeneities.

Atmospheric corrosion is perhaps the most common example of uniform corrosion. Another example commonly found is the corrosion of steel in acidic media. In principle, uniform corrosion could lead to failure in a piece of equipment or structure, due to reduction in thickness. Nonetheless, since it is easily detected and

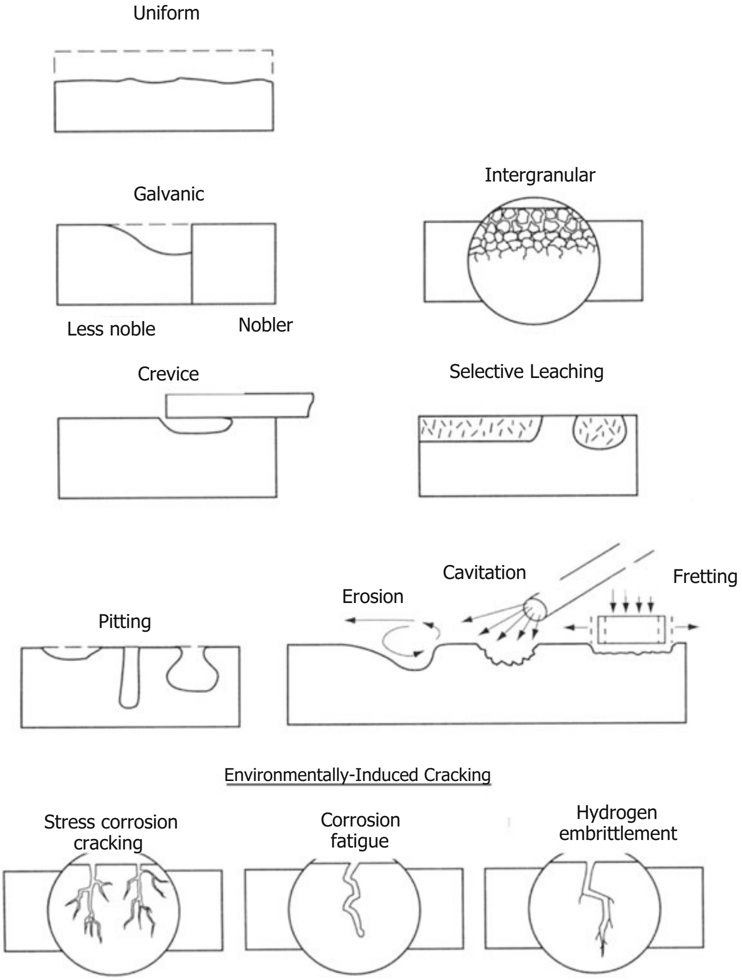


Fig. 15.4 Diagram of the different forms of corrosion (adapted from [2])

it degrades the appearance of materials, this type of corrosion is normally repaired before there are any structural risks. On the other hand, the life of a piece of equipment can be estimated based on simple measurements, which give a quantification of the loss of thickness (mm/year) or loss of mass (mg/day/dm^2) due to corrosion.

When choosing a metal for use in a corrosive medium, a metal that corrodes uniformly in that medium, with a low corrosion rate, should be chosen. Compared to localized corrosion, which is more difficult to foresee, detect, and avoid, uniform corrosion is preferred from an engineering project perspective because its effects can be predicted and quantified during the design stage. Taking the example of an engineering structure, it is possible to specify a *corrosion allowance*, making it

Fig. 15.5 Example of uniform corrosion (photograph by the author)

thicker than necessary so that at the end of its life it will still have the necessary dimensions for mechanical strength and appropriateness for the other functions it was designed for.

15.3.2 Galvanic Corrosion

When two dissimilar metals are placed in contact in the presence of an electrolyte, the difference in potentials between them causes an electrical current to flow: the metal with the lower potential will work as the anode, tending to corrode faster, while the metal with the higher potential becomes the cathode, its corrosion attack being reduced, so it normally becomes protected from corrosion. Galvanic corrosion can, therefore, be recognized by the occurrence of increased corrosion of the less noble metal in the joints of dissimilar metals (Fig. 15.6).

In principle, different materials or alloys will always have different potentials in a given medium. Forecasting the behavior of a certain bimetallic couple can be done based on electrochemical series or, preferably, on galvanic series, since these are obtained for each corrosive medium, and therefore phenomena such as passivation in a specific medium, which substantially alter the behavior of a metal, can be taken into account. In fact, the behavior of the same bimetallic couple can vary drastically depending on its working conditions, which is the case of polarity reversal in steel/zinc pairs that occurs in galvanized materials, for example. In an aqueous medium at low temperatures, zinc corrodes and steel acts as the cathode, being protected. Above 60 °C, however, the polarity of the galvanic pair is reversed, and steel corrodes. This phenomenon, responsible for cases of premature deterioration in galvanized steel pipes used to carry hot water, is explained by the formation of oxide films on zinc at high temperatures, turning this metal passive and, thus, making it nobler.

Fig. 15.6 Example of galvanic corrosion in cast iron piping for water supply due to galvanic coupling with copper indoor piping, in *Corrosion Atlas* (case 01.14.14.01) [5]

Galvanic corrosion tends to be found mainly in the close vicinity to the junction between the dissimilar metals. In fact, one of the steps involved in the corrosion process is the ionic current flow over the corrosive medium, which is normally a slow step, so the length of the respective path tends to be reduced. This effect may be accentuated in situations where the resistance of the electrolyte is very high, such as in very pure waters or atmospheric exposure.

Another very important factor in galvanic corrosion is the ratio of cathodic to anodic areas. Given that the electrons consumed in the cathodic process must be produced in the anodic process, the presence of cathodes with a high area and anodes with a small area leads to very risky situations. To feed the cathodic process, the small anodes have to corrode at a high rate (high current densities), which can even cause the metal to be completely consumed. Conversely, situations in which the anodic areas are much greater than the cathodic areas are not particularly dangerous. Taking as an example two steel plates joined by copper rivets and immersed in seawater, we find that the steel plates undergo only slight corrosion. On the other hand, two copper plates joined by steel rivets would lead to corrosion rates so high in the steel rivets that they would end up being completely destroyed, placing the entire structure in risk. Therefore, if rivets, bolts, or welds are used in a metal structure and are made of a material different from that used for the structure, they should always be made from a more noble metal.

It should be noted that galvanic corrosion is the basis for quite a common anticorrosive protection method—cathodic protection by sacrificial anodes. In this method, the structure to be protected is coupled with a low-nobility metal such as zinc or magnesium. This metal has a greater tendency to oxidize than the other metal, and turns the structure into a cathode, thereby protecting it.

Methods for preventing galvanic corrosion should start by avoiding the use of metals with very different potentials in the galvanic series or, if they must be used, unfavorable cathodic to anodic area ratios should be avoided (cathodes should be small and anodes large). Whenever possible, contact between the two metals should be avoided, using insulation. It is also recommended that coatings are applied and kept in good condition, above all those used on the anode. In some cases, cathodic protection may be chosen, protecting both metals through the use of a third, less noble metal or by applying an impressed current (see Sect. 15.4.4).

15.3.3 Pitting Corrosion

Pitting corrosion is a form of localized corrosion that leads to the formation of small holes that may reach considerable depth (pits), and may be difficult to detect—Fig. 15.7. It occurs in passive materials in the presence of certain aggressive ions, such as halides and, in particular, chlorides.

Among the metals most susceptible to pitting corrosion are stainless steel, aluminum (and its alloys), and iron, which makes it one of the most dangerous types of corrosion. In fact, materials normally considered resistant to corrosion, such as stainless steels, owe their resistance to the formation of a natural film of oxides and hydroxides that protect them from the corrosive medium. However, it is precisely in these materials that pitting corrosion occurs through localized attack of the passive film.

Once pitting has begun, a corrosion cell is formed where the anode is located within the pit, whereas the cathode is the external surface of the metal, covered by the passive film. Once again, this produces a highly unfavorable cathodic to anodic area ratio, which quickly leads to the formation of deep pits. The lower the density of the pits, the more unfavorable the area ratio, so a single pit can grow and deepen

Fig. 15.7 Example of pitting corrosion, in *Corrosion Atlas* (case 04.06.12.02) [4]

much more quickly than many small pits, and the latter is a much less dangerous situation.

A material's susceptibility to pitting corrosion may depend on many factors, among which its composition (and, in particular, the presence of certain alloying elements), its microstructure (heterogeneities are preferred points for the formation of pits), and the characteristics of the corrosive medium, such as the concentration of aggressive ions, pH, or temperature.

In project design, a material should be chosen that is known for not undergoing pitting corrosion in the medium in question, using information available in tables or databases for materials selection. Among stainless steels, some are more resistant to pitting corrosion than others. For example, adding 2 % Mo to 18-8 (AISI 304) stainless steel leads to 18-8Mo (AISI 316) steel, which is much more resistant to pitting (316 SS is often used in seawater, unlike 304). Generally speaking, the following materials can be classified in increasing order of resistance to pitting corrosion: AISI 304 < AISI 316 < Hastelloy (Ni/Cr), Nionel (Ni/Cr/Fe) < Superaustenitic stainless steels (20Cr–18Ni-6Mo-0.2Ni) < Superferritic stainless steels (30Cr-4Mo) < Titanium.

15.3.4 Crevice Corrosion

Crevice corrosion is also a form of localized corrosion that occurs in areas with small volumes of stagnating solution that is barely renewed or oxygenated, such as in crevices between two metal surfaces or under deposits (of sand, dirt, mud, limestone, rubble, etc.). A small area of metal (in the crevice or under the deposit) becomes depleted in oxygen and begins to corrode, while the remaining surface continues to be easily oxygenated, behaving as a cathode for the system (Fig. 15.8). The attack is made worse by the unfavorable ratio between a large cathodic area and a small anodic area.

As in pitting corrosion, crevice corrosion involves localized destruction of the oxide film, and it is therefore characteristic of passive materials. Nonetheless, crevice corrosion does not need the presence of aggressive ions, although it can be accelerated by them, and so it can occur in media as different as chlorides, sulfates, nitrates, etc. On the other hand, activating this type of corrosion is easier than pitting corrosion (the critical potential needed for crevice corrosion to occur is lower than that for pitting corrosion). Therefore, and from an engineering perspective, there are no doubts that the crevice corrosion of stainless steels in seawater is more important than pitting corrosion.

Preventing crevice corrosion involves, above all, avoiding the presence of crevices in joints. In order to ensure this, continuous welding should be used rather than rivets or bolts and existing joints should be covered with overlapping material (e.g., solder). The equipment should also be designed so as not to create occluded areas favorable to the accumulation of stagnant liquid and appropriate coatings should be used. Correctly selecting the materials is also fundamental. For example, among the stainless steels, AISI 316 and AISI 316L (both containing Mo) have

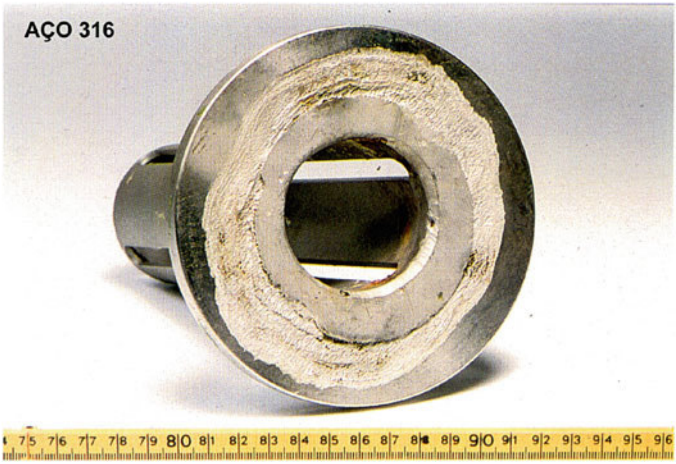


Fig. 15.8 Example of crevice corrosion of AISI 316 stainless steel flange in *Corrosion Atlas* (case 04.06.13.02) [4]

greater resistance to crevice corrosion than AISI 304, although under certain conditions they may still be attacked.

On the other hand, equipment should be inspected at appropriate intervals, removing deposits that may create crevices. In the case of pipelines or storage tanks, solids in suspension that can create those deposits should also be removed.

15.3.5 Filiform Corrosion

Filiform corrosion may be considered a particular case of crevice corrosion that consists of formation of very fine filaments that propagate throughout the surface. It occurs frequently in painted, enameled, or lacquered surfaces, causing the coating to peel away (Fig. 15.9). It can be said that filiform corrosion does not substantially affect the physical properties of the metal, so it does not pose risks to the stability or safety of the structures affected. However, filiform corrosion may become particularly problematic in the production of food or beverage cans, since it degrades the appearance of the products, leading consumers to avoid them and, thus, affecting sales.

The prevention of filiform corrosion involves using brittle coatings (that break when a new filament is started, avoiding its growth) or coatings that are less permeable to water and storing painted materials in environments with low humidity levels.

15.3.6 Selective Leaching

Selective leaching consists in the preferential dissolution of an alloying element. The most common situation is selective leaching of brass (Cu and Zn alloy), also

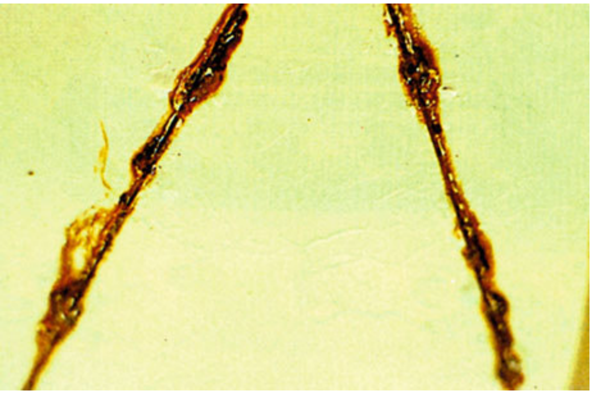


Fig. 15.9 Example of filiform corrosion under a paint layer (note the filaments starting at the rusted scratches) [6]

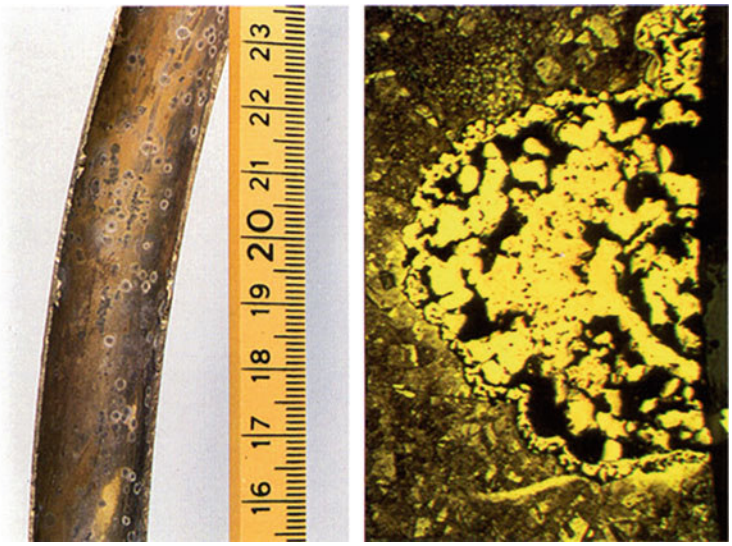


Fig. 15.10 Example of selective leaching of brass, in *Corrosion Atlas* (case 06.05.16.02) [4]

known as dezincification, but similar processes may occur in other alloys, with selective removal of aluminum, iron, cobalt, chromium, etc.

The selective leaching of brass is especially important in civil construction because of the wide range of applications of this material, especially for decorative purposes. Since common yellow brass is an alloy with approximately 30 % zinc and 70 % copper, and given the low nobility of zinc, this alloying element corrodes while copper remains, leaving the material brittle and porous. This type of corrosion is easily detected as the corroded zones assume a red color (typical of copper) that contrasts with the yellow of the original brass. Therefore, selective leaching of brass heavily degrades the appearance of the material, compromising its function and aesthetic (Fig. 15.10).

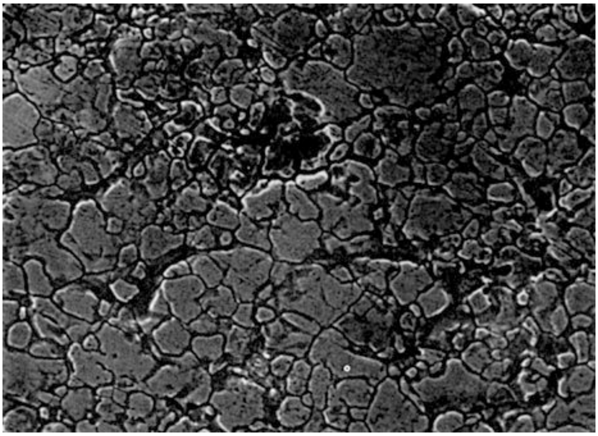


Fig. 15.11 Intergranular corrosion of austenitic stainless steel, observed through a scanning electronic microscope (Figure 1.13 in [2])

Prevention of selective leaching can be achieved by reducing the aggressiveness of the environment or selecting less susceptible materials. For brass, a protective varnish can also be applied.

15.3.7 Intergranular Corrosion

Intergranular corrosion is also a localized form of attack, in which a narrow zone at and adjacent to grain boundaries of a metal alloy is corroded whereas little or no corrosion is found at the grains. This type of corrosion is due to the formation of corrosion microcells at the grain boundaries (Fig. 15.11). As corrosion propagates, the material's mechanical properties are deeply affected and fracture may occur under mechanical load.

The most common form of intergranular corrosion is the one observed in austenitic stainless steels. When they are welded, the different areas of the structure are heated to different temperatures, depending on their distance to the weld. In the areas subjected to temperatures of 450–800 °C, it may occur that part of the chromium situated close to the grain boundaries combines with carbon, forming $Cr_{23}C_6$ and leaving areas around the grain boundaries depleted in chromium (Fig. 15.12). As a minimum chromium concentration of approximately 10 % is needed for a steel to become "stainless," the depletion of chromium to values below this threshold around the grain boundaries will lead to intergranular corrosion—it can be said that the alloy is sensitized, so this type of corrosion is also called the sensitization of austenitic stainless steels (Fig. 15.13).

Preventing this type of corrosion can be done by heat treating the piece after welding, which involves heating it above sensitization temperature, followed by rapid cooling (solution-quenching). In this case, at high temperatures, the

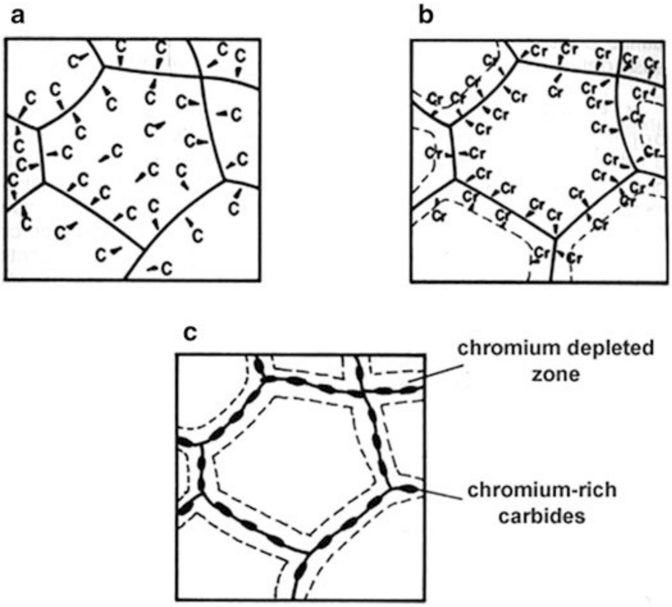


Fig. 15.12 Intergranular corrosion mechanism in austenitic stainless steels [7]

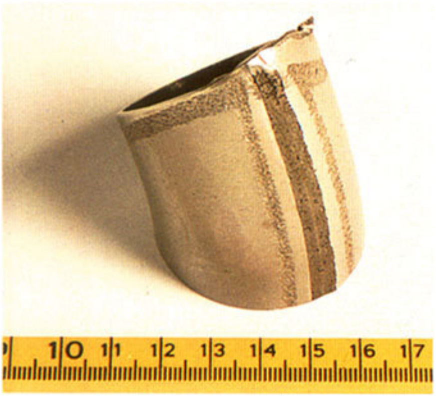


Fig. 15.13 Example of sensitization of austenitic stainless steels, in *Corrosion Atlas* (case 04.01.19.01) [4]

chromium carbides formed can be dissolved and, with fast cooling, there is no time for carbides to be formed again. Stainless steels with a carbon content of less than 0.02 % can also be used—"extra low carbon steel"—such as AISI 304L or 316L. Alternatively, alloying elements that have a greater affinity to carbon (stabilizers), such as titanium and niobium (the latter also known as columbium), may be added (during manufacture), resulting in stainless steels such as AISI 347 and 321. When added in sufficient quantity, they combine with the available carbon, avoiding the formation of chromium carbides.

15.3.8 Environmentally Induced Cracking

Certain properties of metals and alloys (ductility, tensile strength, etc.) are practically unchanged by the environment and, for example, it is possible to specify tensile strength of a material without referring to the medium in which it will be used. Also certain corrosion phenomena (galvanic corrosion, pitting corrosion, etc.) are unaffected by mechanical forces, and the corrosion rate of a steel, for example, can be given without mentioning the mechanical stresses applied to the material.

There are, nonetheless, situations in which there is a strong interaction between the corrosive environment, stress, and their effects in terms of corrosive attack. The term used, therefore, is environmentally induced cracking, which includes, generally speaking, different phenomena, such as stress corrosion cracking, corrosion fatigue, fretting corrosion, erosion corrosion, cavitation corrosion, and hydrogen embrittlement. Afterwards, a short description of the two first and the last type is given, since the occurrence of the others in civil engineering structures is relatively rare.

In *stress corrosion cracking* (abbreviated to SCC), there is a synergetic action between stress and the corrosive medium, so fracture occurs in a shorter amount of time than expected for the sum of the independent effects of stress and aggressive medium. Not all the metal/medium combinations are susceptible to SCC, which makes it a process that is extremely dependent on the characteristics of the material/medium/stress combination (Fig. 15.14). Since it is a localized phenomenon, most of the material is not affected, while in some places cracks form that progress through the metal or alloy (Fig. 15.14). On the other hand, and since it happens in passive materials, in which the overall corrosion rate is very low, there is practically no loss of mass in the material, and it remains in apparently good condition until the moment when the fracture can be seen. The compositions and structures of affected alloys, as well as the properties of the media involved, can be so different that it is not possible to find a single mechanism that explains this type of corrosion.

Fig. 15.14 Illustration of the dependence of characteristics in the combination of material/environment/stress in stress corrosion cracking (SCC) and example of SCC in a stainless steel knife (photograph by the author)

A classic case of SSC is "season cracking," observed on brass cartridge cases of military forces in the tropics (originally reported by the British forces in India). During periods of heavy rainfall, the cartridges often showed cracks, especially where the case was crimped to the bullet. The environmental component responsible for this process was found to be ammonia, resulting from decomposition of organic matter, whereas the zone attacked was the one submitted to higher residual stresses.

Preventing SCC can be achieved by decreasing stress to values below the minimum limit for SCC (if this limit exists), by eliminating critical species in the corrosive medium (degasification, demineralization, distillation), by replacing the alloy with another less susceptible to SCC (often mild steel is more resistant to SCC than stainless steels), by using coatings (that avoid contact between the metal and the environment), or even by using shot peening, which produces residual compression stress in the surface of the metal.

When a component is subjected to cyclic stresses in a corrosive medium, the conditions are found for the occurrence of *corrosion fatigue*. Corrosion fatigue differs from mechanical fatigue (without corrosion) because of the intervention of an aggressive medium, which makes the material more susceptible.

The distinction between a fatigue fracture and a fracture caused by corrosion fatigue is generally easy to make: in mechanical fatigue (without corrosion), the region at the start of the fracture has a smooth appearance, due to the friction undergone in successive cycles during formation, followed by a second area with a rough appearance, due to a brittle fracture (arising from the metal's ultimate strength having been exceeded, by reducing the area of the cross section); conversely, in corrosion fatigue, the first area of fracture is covered by the products of the corrosion, but there is still a rough part corresponding to the brittle fracture (Fig. 15.15).

In corrosion fatigue, there is an accentuated dependence on the aggressiveness of the corrosive medium: the propagation rate is much higher in aggressive media (e.g., seawater vs. air) and the presence of a corrosive medium also reduces the time needed for cracking to begin. Contrarily to what is observed in ordinary fatigue, the stress-cycle frequency has a marked influence on the corrosion fatigue resistance, with lower frequencies resulting in more severe corrosion, which may be explained based on the greater contact time between the metal and the environment in this case. On the other hand, there is low specificity in what concerns the corrosive medium: any environment that corrodes a metal reduces its resistance to fatigue, making it more likely to occur, so all the variables that define the aggressiveness of the medium (pH, temperature, oxygen content, etc.) have an influence on the process.

Preventing corrosion fatigue may be achieved by reducing cyclic forces and/or the aggressiveness of the environment. Therefore, the intensity of the alternated stresses can be reduced or the design of the parts modified, avoiding points where stresses accumulate, such as holes or notches. Other alternatives include replacing the alloy by another less susceptible to corrosion and/or fatigue, using heat treatments, which release metals from residual stresses, or even using shot peening,

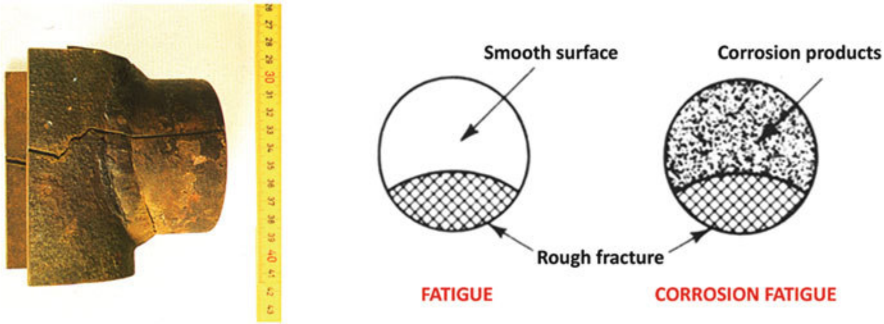


Fig. 15.15 Example of corrosion fatigue (platform support in carbon steel, subjected to oscillations and in contact with naphtha), in *Corrosion Atlas* (case 01.11.28.01) [4], and distinction between fracture caused by fatigue and fracture caused by corrosion fatigue

which produces residual compressive stresses on the surface of the metal. The influence of the medium can be mitigated by using corrosion inhibitors or using metallic coatings (zinc, chromium), provided that they do not introduce considerable stresses.

Hydrogen embrittlement arises from the action of hydrogen on metal structure. Hydrogen, in its atomic form (H), has dimensions that are so small that it easily penetrates and diffuses into the metal lattice, where its presence leads to the deterioration of mechanical and metallurgical properties.

Atomic hydrogen is an intermediate of the H^+ reduction reaction that accompanies a corrosion process:

$$2H^+ + 2e^- \rightarrow 2H \rightarrow H_2 \tag{15.8}$$

Most atomic hydrogen tends to combine, forming molecular hydrogen gas. Nonetheless, in the presence of “poisons” such as sulfide, cyanide, or antimony ions, as well as elements such as bismuth, lead, selenium, or arsenic, the formation of molecular hydrogen is inhibited, so the concentration of H at the surface increases, facilitating its penetration into the metal. The presence of hydrogen sulfide (H_2S), for example, is especially dangerous, since it not only provides the sulfide ion (poison) but also provides H^+. Atomic hydrogen may also originate from atmospheres rich in hydrogen, for example, during heat treatments or welding, or as the result of applying cathodic protection (see Sect. 15.4.4).

In civil engineering, the simultaneous presence of hydrogen and applied stress may be particularly deleterious to the metal, as it happens in cathodic protection of prestressed concrete. In this case, it is believed that hydrogen is absorbed at the bottom of preexisting voids, and when it builds up it creates distortion and a loss of cohesion in the crystal lattice. At the bottom of the crevice, hydrogen reacts with the metal, forming an area of brittle metal hydride that breaks, causing the crevice to advance.

Preventing hydrogen embrittlement can involve choosing more resistant materials or applying heat treatments that remove the accumulated hydrogen. Modification of the corrosive medium may also be effective, by removing sulfides or other poisons or by increasing pH, or even by eliminating the sources of hydrogen (avoiding the use of cathodic protection or the presence of galvanic pairs), or by applying a hydrogen-impermeable coating.

15.3.9 Biological Corrosion

Biological corrosion consists of the deterioration of a metal by corrosion processes that directly or indirectly arise from the activity of living organisms. These organisms may be microorganisms (like bacteria) or macroorganisms (like algae, fungi, barnacles, or mussels). As they live and reproduce in a wide range of pH values, temperatures, or pressures, biological corrosion can be found in numerous environments.

The chemical reactions that are involved in the metabolisms may influence the corrosion processes, directly affecting anodic and cathodic reactions, altering protective films, creating conditions (media) with high corrosivity or producing deposits. It can be said, therefore, that biological corrosion is not, in itself, a separate type of corrosion: what characterizes it is the intervention of living organisms that produce the conditions necessary for the occurrence or acceleration of a certain type of corrosion.

In the case of corrosion caused by the presence of microorganisms (microbiologically influenced corrosion, MIC), prevention can be achieved by coating buried structures with plastic tape, enamel, asphalt, or concrete (it should be noted that certain aerobic bacteria, such as sulfur-oxidizing bacteria, can destroy concrete by making the medium acidic through the production of sulfuric acid). Cathodic protection can also be used, especially in conjunction with coatings. Aeration (used, e.g., in effluents) or, in recirculation systems, the use of inhibitors or germicides such as chlorine or chlorine compounds can also be effective.

Corrosion caused by macroorganisms can be avoided through the use of antifouling paint that contains toxic substances (copper compounds, tin. . .), which act as poisons, impeding the macroorganisms to attach to the surface. Nonetheless, because of their environmental impact, these paints are being abolished. In submerged structures, ultrasound can be used, and some agents can be used in closed circuits, such as chlorine and chlorine compounds. Periodically cleaning is mandatory to avoid obstruction of flow and/or occurrence of crevice corrosion.

15.3.10 Polymer Corrosion

Polymers do not corrode electrochemically like metals, but they do degrade through swelling, loss of mechanical properties, softening, hardening, discoloration, etc.

The wider definition of corrosion (deterioration of a material through action of the surrounding environment) may thus be applicable to polymer deterioration.

Like metals, polymers can be subjected to SCC: the joint effect of a chemical agent and an applied stress may lead to fracture, which would not happen so easily under the individual action of each one of these agents. Examples of this attack include polystyrene, poly(methyl methacrylate) (Perspex), and polyethylene, in media such as oxidizing acids, organic solvents, etc.

Elastomers can also lose their properties through action of the environment, as in rubber embrittlement caused by ozone (ozone cracking), which can be avoided by adding antioxidants.

A particular and highly important example of polymer corrosion is degradation by ultraviolet radiation. This radiation, which represents 4 % of the sun's natural radiation, has enough energy to break some of the main types of bonds found in polymers (C–N, C–C, C–O, N–H, and C–H). Although only a small number of bonds are broken, and they are located at the surface (because the light does not penetrate more than 0.5 mm), its effects are felt in the polymer's mechanical, physical, and chemical properties.

This type of corrosion can be avoided by using polymeric coatings (which also have a limited lifespan), by adding antioxidants to the polymer (which consume the O_2 necessary for the degradation reaction) or even by adding ultraviolet absorbers that, as the name suggests, absorb ultraviolet radiation, releasing it (through fluorescence or phosphorescence) in the form of lower energy radiation (visible or infrared) that is not enough to break the chemical bonds.

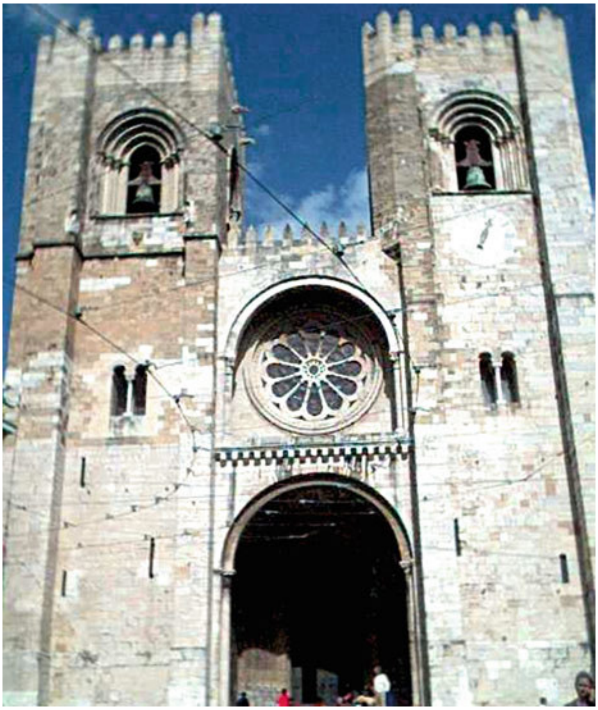
15.3.11 Corrosion of Stone

Like in the previous section, this process is not an exclusively electrochemical phenomenon, and it is often defined as *stone decay*. The historical, cultural, and economic importance that many structures made of geological material have in society and the need to preserve them justify the growing interest in this area. The deterioration mechanism for stone is very complex, since it involves both chemical and electrochemical processes (controlled by climate parameters), which lead to mechanical, structural, and aesthetic changes in the material.

Among the main causes of stone decay, one can highlight climate parameters, natural disasters, biological action (organic and inorganic detritus from the metabolisms of living organisms), and human activity (pollution, vibration, hole drilling, vandalism, and graffiti).

In urban areas, stone ageing is greatly accelerated by the detrimental effects of air pollution. Among the main pollutants found in the air, sulfur dioxide (SO_2) and nitrogen oxides (NO_x) have the particular characteristic of being able to oxidize, producing acidic species. These species, when in contact with stone, cause the calcium carbonate (one of its main components) to dissolve, leading to aesthetic changes and progressive deterioration of the material—Fig. 15.16. This phenomenon is boosted by successive wet/dry cycles, since the crystallization of the salts

Fig. 15.16 Lisbon Cathedral: aesthetic changes due to air pollution



produced generates internal stresses that lead to cracking and disaggregation in the material.

15.4 Anticorrosive Protection Methods

Anticorrosive protection may be achieved through five different ways: appropriate selection of materials, adequate design of the parts, modifying the corrosive environment, modifying the system's potential, or applying coatings.

15.4.1 Materials Selection

The selection of materials should take into account the purpose for which they are to be used, in order to choose the material that has the best resistance in the environment to which it will be exposed. To obtain the appropriate material/medium combination, databases are used, available in different formats, as tables in books, diagrams, or computer programs.

When different materials are combined, it is particularly important to ensure that no galvanic couples are formed, and if this happens, that galvanic corrosion does not put the structure's integrity at risk. For example, for materials exposed to a

Table 15.2 Galvanic series in seawater

Nobler
↑
Platinum
Gold
Graphite
Titanium
Silver
Zirconium
Stainless steels AISI 316 and 317 (passive)
Stainless steel AISI 304 (passive)
Stainless steel AISI 430 (passive)
Nickel (passive)
Cupronickel (70–30)
Bronze
Copper
Brass
Nickel (active)
Tin
Lead
Stainless steels AISI 316 and 317 (active)
Stainless steel AISI 304 (passive)
Cast iron
Steel or iron
Aluminum alloy 2024
Cadmium
Aluminum alloy 1100
Zinc
Magnesium and magnesium alloys
↓
More active (*less noble*)

marine medium, the respective galvanic series of metals should be considered (Table 15.2), seeking combinations of metals that have close positions in this table.

If it is difficult to make the use of metals or metal alloys compatible with the environment to which they will be exposed, non-metal materials can be chosen, such as rubbers (natural or synthetic), plastics, ceramics, carbon and graphite, or wood, provided that their physical properties are appropriate for the purpose.

15.4.2 Design

Many risk situations can be avoided by correctly designing parts and structures. The criteria to be used should avoid the occurrence of any type of corrosion, requiring that the designer (or team) has some knowledge on corrosion phenomena and mechanisms.

Generally, situations in which liquids accumulate or that favor the creation of crevices or galvanic pairs are to be avoided. High mechanical stress should also be avoided, as well as the use of pipes with tight curves (erosion corrosion). The need for maintenance of the structures (painting, cleaning) should be foreseen, ensuring that the size of the structures allows it to take place and safeguarding the possibility of repairing or replacing parts. When designing structures that may deteriorate, it is also advisable to make allowances for the future reduction of thickness caused by corrosion. A set of practical rules to be followed when designing structures and equipment is shown in Fig. 15.17.

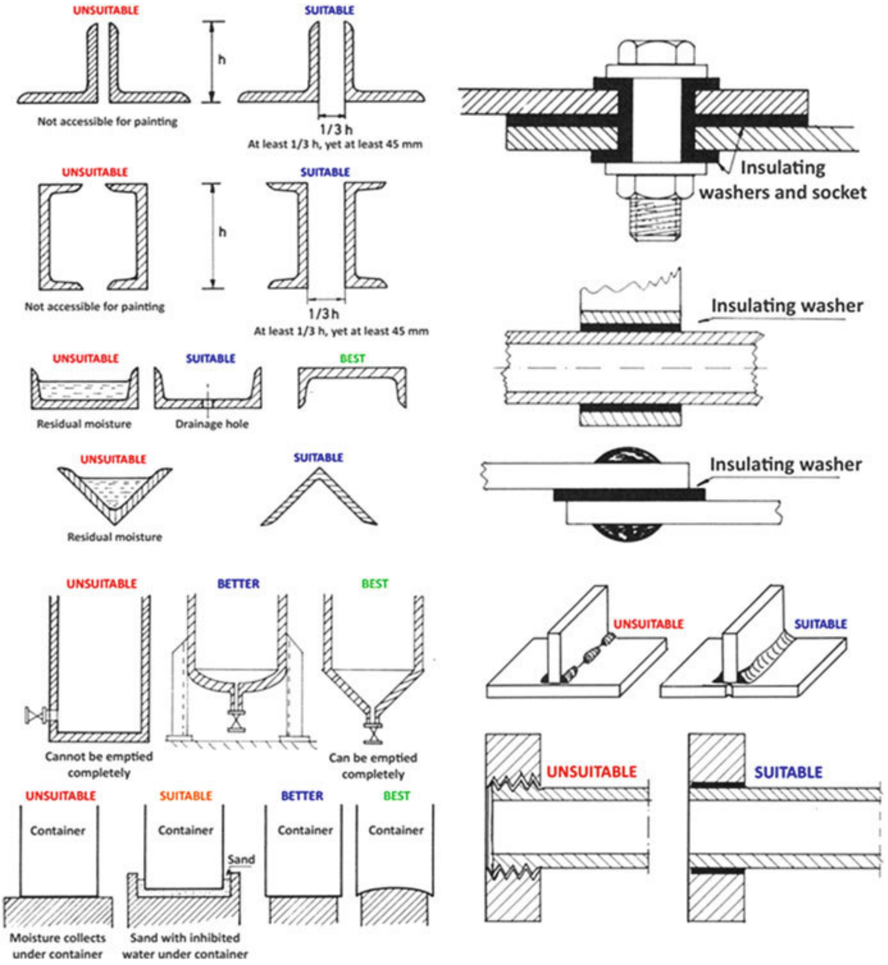


Fig. 15.17 Rules to be followed when designing structures and equipment (adapted from [8])

15.4.3 Changing the Corrosive Environment

Modifying the characteristics and aggressiveness of the corrosive medium can be achieved in several ways, including lowering temperature, reducing the speed of fluids, changing the concentration of corrosive agents, and removing oxygen and oxidants. Nonetheless, not all systems react to changes in the same way (sometimes reducing the temperature or flow rate can lead to more severe attack), besides which, in most cases, it is not possible to implement any of these actions because the characteristics of the medium cannot be changed (this is the case for atmospheric or seawater exposure or in drinking water piping).

In many cases the anticorrosive protection may be achieved through the use of *corrosion inhibitors*, substances that, when added in adequate (normally small) concentrations to the corrosive medium, decrease the corrosion rate. Corrosion inhibitors can be classified into one of three categories:

- Anodic inhibitors, which delay or eliminate anodic reactions. These inhibitors are anions that migrate to anode surfaces, where they normally react with corrosion products, forming an adherent, insoluble, and protective film on the surface of the metal. This process leads to an increase in anodic polarization and an accentuated reduction in corrosion rate. Among the best known anodic inhibitors, we find chromates and salts of alkaline metals, such as carbonates, silicates, borates, nitrites, nitrates, and phosphates.
- Cathodic inhibitors, which delay or eliminate cathodic reactions. These inhibitors generally provide metal cations that react with hydroxides produced in the cathodic reaction, leading to the formation of a film that is deposited on the cathodic areas, stopping the cathodic process and, by consequence, not allowing the anodic process of corrosion to take place. For example, zinc, magnesium, and nickel sulfates react with hydroxides, forming $Zn(OH)_2$, $Mg(OH)_2$, and $Ni(OH)_2$, respectively. These products, which are insoluble, are deposited in the cathodic areas, leading to an accentuated increase in cathodic polarization. Often, to increase the efficiency of inhibitors, a mixture of cathodic inhibitors and anodic inhibitors is used, provided that they are not chemically incompatible.
- Mixed inhibitors, which adsorb over the material to be protected, creating a protective film that covers both anodic and cathodic areas. These are generally organic inhibitors, as amines, alkanolamines, and carboxylic acids, which are quite effective, their use having been increasing.

15.4.4 Modifying the System Potential (Cathodic Protection)

Cathodic protection is an electrochemical anticorrosion technique that consists of displacing the potential of the system in the negative direction, reducing or completely preventing the oxidation of the metal. This is done by supplying electrons to the metal structure, making it behave as a cathode. This goal can be achieved in one of two ways: by coupling sacrificial anodes or through impressed currents.

15.4.4.1 Cathodic Protection by Sacrificial Anodes

In this method, a metal (anode) with an electrochemical potential lower than that of the metal to be protected is used (see Table 15.2), allowing a galvanic pair to form, in which the anode corrodes and the material to be protected works as a cathode (Fig. 15.18). In practice, it involves a controlled and beneficial application of galvanic corrosion, in which one metal is sacrificed (the reason behind the name *sacrificial anode*) to protect another. Since the anode is dissolved, it must be replaced regularly.

The most commonly used metals for making anodes are magnesium, zinc, and aluminum. Anodes should meet a series of requirements, including: (1) good theoretical and practical current yield with respect to the mass consumed and (2) the current should not diminish over time (e.g., due to the formation of passive films). Magnesium, which is an extremely reactive material, is frequently used for protection in soils or in pure water (e.g., hot water, when protecting electric water heaters), since the high resistance of those media prevents the anodes from being consumed too quickly. However, it should not be used in seawater, whose high conductivity would lead to fast consumption with a very low efficiency. In marine media, it is more common to use aluminum, because of its low price. Aluminum, when pure, may become passive, reducing its functionality, but adding small percentages of zinc or mercury was found to overcome that limitation, and alloys were obtained that remain active in seawater. Due to environmental concerns, the use of zinc and mercury has been reduced for this purpose, and new aluminum alloys obtained by the addition of tin, bismuth, or indium are now being used.

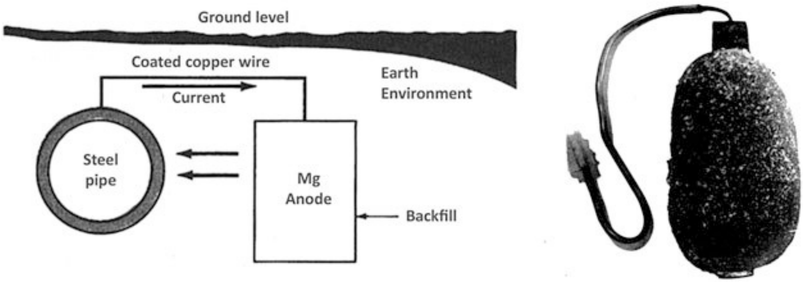


Fig. 15.18 Cathodic protection system using sacrificial anodes (adapted from [9]) and photo of a magnesium anode [6]

15.4.4.2 Impressed Current Cathodic Protection

Cathodic protection by impressed currents uses inert anodes (which do not corrode) to create a current flow using an external source or rectifier (Fig. 15.19).

The level of protection depends on the applied potential. Therefore, if the potential is only slightly lower than the corrosion potential of the metal, the anodic reaction continues, although at a lower rate. Effective protection, in theory, should lead to total elimination of the anodic reaction of metal dissolution, corresponding to driving the potential of the metal to a value equal or below the equilibrium potential of its oxidation reaction. If these principles appear to be simple, their application does, however, involve some difficulties. In fact, applying a cathodic potential for reducing the rate of the anodic reaction, at the same time accelerates the cathodic reaction, which may lead to hydrogen being released. Although mild steel is not significantly affected by this phenomenon, in prestressed steel the greatest care and vigilance must be observed when applying low potentials, since this material may undergo hydrogen embrittlement. From an economic perspective, the installation costs of cathodic protection systems are high but the technique is considered by many to be the most efficient method for protecting metallic materials.

Several materials can be used as anodes in cathodic protection with impressed currents. Given that in this case, polarization is not achieved through anode dissolution but through an external current, it is important to choose a material that allows the anodic reactions to develop at the surface without damaging it (in this way, the anodic reactions will involve the oxidation at the anode of species from the surrounding environment and not oxidation of the anode). Over time, several metals have been used as anodes, from cast iron and steels to carbon and even graphite. The most appropriate material for this function would be platinum, but its high cost made it impracticable for many years. Recently, developments in metallization techniques have made it possible to manufacture platinum-plated titanium anodes, in which titanium is coated with a very thin surface layer (1–5 μm) of platinum. Bringing together the good mechanical properties of titanium and the platinum coating's excellence as an anode, this material quickly became the most widespread in cathodic protection for immersed systems, because although its initial cost may be a little higher, its durability and efficiency are much greater than alternative materials.

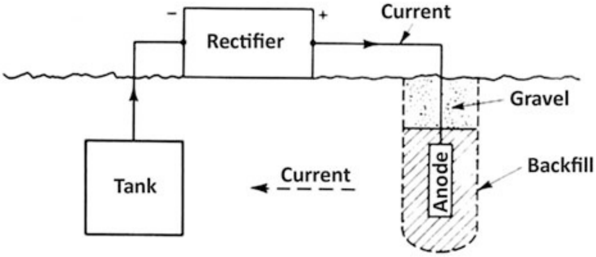


Fig. 15.19 Cathodic protection system using impressed currents (adapted from [9])

15.4.5 Coatings

A coating is a protective layer that is formed naturally or artificially between the metal and the aggressive medium. For example, the high resistance to corrosion of stainless steels and aluminum is the result of the spontaneous formation of a protective film rich in Cr_2O_3 or Al_2O_3, respectively. Regardless of the process for forming the coating, its future efficiency is heavily conditioned by the preparation of the surface. Therefore, the cleaning and preparation process for the surface are fundamental to obtaining adherent, uniform coatings. Protective coatings may be metallic or nonmetallic.

15.4.5.1 Metallic Coatings

These coatings aim to form a metallic layer over a certain material and can be used for decorative purposes (gold, silver, nickel. . .), to increase resistance to friction and abrasion (indium), to harden the surface (chromium plating), or to increase resistance to corrosion (chromium plating, nickel plating, galvanizing, tin plating. . .).

A metal coating may be produced by several processes, such as electrodeposition (or electroplating), thermal spraying (metalizing), cladding, hot dipping (such as the case of zinc coating of steel through galvanizing), surface alloying (or diffusion), electroless deposition, or advanced methods, such as those involving vacuum techniques (chemical or physical vapor deposition, ionic implantation. . .).

The protection obtained by the use of a metallic coating can be just due to a physical barrier effect between the metal and the environment or involve active protection. In the first case, protection is achieved because the coating material is nobler than the substrate, that is, it is more resistant to the aggressive medium. In this case, the protection will be effective while the coating is intact. However, these coatings should be free from flaws; if this is not the case, a galvanic cell will form between the coating and the substrate, the latter corroding quickly because it is less noble and has a small area.

When coatings are used that are less noble than the substrate, protection is achieved through the combined effect of the physical barrier and cathodic protection by sacrificial anodes. In this case, the presence of flaws is not serious, since the coating will behave as an anode, while the substrate behaves as a cathode, and remains protected until the coating is consumed.

The choice of a particular metal coating should be made according to its chemical stability in the environment to which it will be exposed. For example, galvanized steel has good resistance to corrosion in neutral or acidic media, but low resistance in basic media, since zinc dissolves in high pH environments. Galvanized steel should not be used to transport hot water at temperatures higher than 60 °C, since polarity reversal of the zinc/steel couple would trigger the corrosion of steel (this phenomenon is a common cause of early deterioration in hot water piping, see Sect. 15.3.2).

15.4.5.2 Nonmetallic Inorganic Coatings

These coatings consist of an inorganic film formed over the surface of the material to be protected. They include enamels, ceramics, composites, glasses, porcelains, oxides, carbides, chromates, nitrides, and silicides. Coatings formed over the surface to be protected should be uniform and have good adherence, in order to effectively protect the metallic substrate in aggressive media. The most widely used coating processes of this category include anodizing, chromate conversion coatings, and phosphate conversion coatings.

Anodizing, in particular aluminum anodizing, consists in the thickening of the protective film that forms spontaneously over aluminum. Anodizing is an electrolytic oxidation process, in an appropriate solution, in which the material to be treated acts as an anode, oxidizing and forming a thick protective layer of oxides. Besides aluminum, there are other materials, such as magnesium, titanium, and zirconium, which can be anodized in order to increase their corrosion resistance.

Chromate conversion consists of forming a coating from a solution containing chromates or chromic acid. These coatings can be applied directly onto the metal to be protected or over a layer of oxides and phosphates. In addition to their anticorrosive function, conversion coatings can be used to promote the adherence of organic coatings. Given the high toxicity of the chromate ion, whose use is gradually being prohibited, the application of this type of coating should be severely restricted in the near future.

Phosphate conversion allows a layer of phosphates to be applied over oxides and hydroxides native to metal surfaces, such as iron, aluminum, galvanized steel, cadmium, and magnesium. Further to its protective function, this layer also increases the adherence of paints or other organic coatings, being used as a pretreatment, although it may also be used as it is for decorative purposes.

15.4.5.3 Organic Coatings

Organic coatings include a wide range of materials. The most popular are paints and varnishes, which are described in Chap. 17. Painting as an anticorrosive protection technique is easily applied and has an attractive cost/efficiency ratio. Painting systems increase resistance to corrosion through different mechanisms that include the barrier effect, inhibition (anodic or cathodic), and electrochemical protection (cathodic protection). The barrier effect is caused by the fact that the painting system consists of a physical barrier with low permeability that blocks the access of aggressive agents to the substrate. The efficiency of the barrier effect will depend on the thickness of the coating, its homogeneity, and its chemical stability. The inhibition mechanism arises from the presence of pigments that stimulate the formation of a passive layer over the surface of the metal. Among the most common pigments, chromates, phosphates, and titanates stand out. The electrochemical effect is based on the principles of cathodic protection (see Sect. 15.4.4.1), using metallic pigments that should be less noble than the metal to be protected, as happens when a zinc powder-based primer is applied to steel.

Other polymers may be applied to a metallic substrate in order to increase its corrosion resistance. Silicone, plastics, elastomers, rubbers, etc. are all examples.

They have the advantage of being flexible, light and are effective at blocking the water access to the substrate. Nonetheless, they have some limitations, specifically in terms of chemical attack and temperature variations.

There are other coatings with protective characteristics that result from pretreatments involving reactive molecules and the metal surface. Silanes, solgel treatments, and plasma polymerization stand out for their growing importance in the industry.

15.5 Corrosion of Reinforced Concrete Rebars

Rebar corrosion is the main cause of deterioration in reinforced concrete structures. The main agents responsible for corrosion of reinforcing steel are chloride ions and carbon dioxide.

15.5.1 The Chloride Ion

Concrete contamination by chloride ions can occur through the use of inert material and/or water contaminated with chlorides or exposure to the marine environment.

For the corrosion process to start, the free chloride content in the steel–concrete interface must be above a certain value, known as the threshold limit. This value depends on the alkalinity of medium and is higher, the higher the pH. Generally, for concrete made using Portland cement, a $Cl^-/(OH^-)$ ratio of <0.6 is acceptable. Standard BS 8110 limits the total chloride content to 0.4 % mass, relative to the mass of the cement. European standards recommend the same amount.

Below the critical chloride level, the corrosion process does not start, since chlorides have the ability to adsorb on the surface of the cement hydration products, establishing stable chemical bonds with cement, producing chloroaluminate. Later, these chlorides may be released into the solution, if for some reason there is deterioration of the aluminates, as happens, for example, during acid attack [10–12].

Figure 15.20 shows a diagram of the action of the chloride ion on the progression of corrosion in reinforcing steel, and the role played by the cover thickness (the thickness of the layer of concrete between the reinforcement and the exterior). This barrier has a protective role. However, it possesses small pores and defects that allow diffusion of water, chlorides, and oxygen to the steel–concrete interface.

The chloride ions penetrate the passive film through defects and/or damaged areas and lead to the formation of anodes, where the conversion of metallic iron into iron ions (Fe^{2+} and Fe^{3+}) takes place. The electrons released in this process are used at the cathode for oxygen reduction and the consequent formation of OH^- ions. These ions, dissolved in the electrolyte (the aqueous phase that fills the pores in the concrete), combine with the iron ions and lead to the formation of several voluminous iron oxides and hydroxides, in accordance with the chemical reactions shown below:

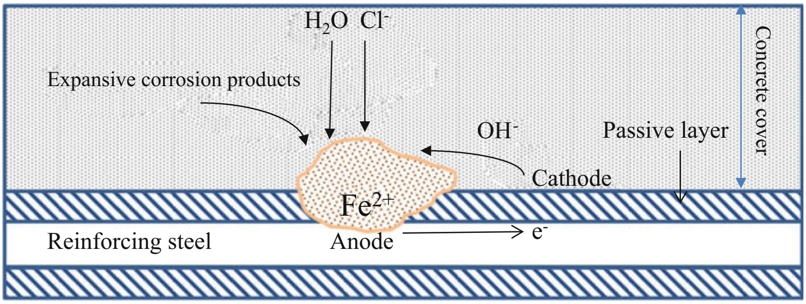


Fig. 15.20 Diagram evidencing the process of reinforcing steel corrosion induced by the chloride ion

Anode:

$$\mathrm{Fe} \rightarrow \mathrm{Fe}^{2+} + 2e^- \tag{15.9}$$

$$\mathrm{Fe}^{2+} + 2\mathrm{OH}^- \rightarrow \mathrm{Fe(OH)}_2 \quad \text{Iron (II) hydroxide} \tag{15.10}$$

$$\mathrm{Fe(OH)}_2 + \mathrm{OH}^- \rightarrow \mathrm{Fe(OH)}_3 + e^- \quad \text{Iron (III) hydroxide (red rust)} \tag{15.11}$$

Cathode:

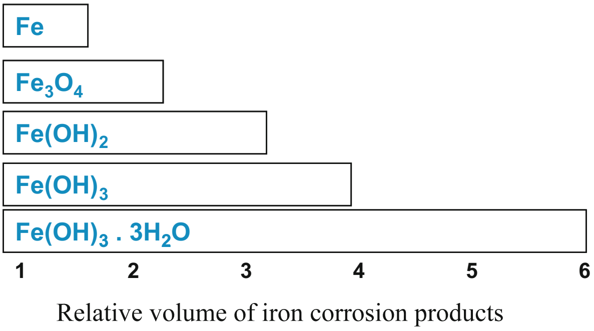
$$4e^- + \mathrm{O}_2 + 2\mathrm{H}_2\mathrm{O} \rightarrow 4\mathrm{OH}^- \tag{15.12}$$

The action of chlorides leads to the development of localized corrosion (pits) on the reinforcing steel. Consumption of the reinforcement, i.e., reduction in its cross section, reduces the steel's tensile strength, and irreparably affects the strength of the entire structure. Conversely, the accumulation of expansive corrosion products (Fig. 15.21) at the interface steel–concrete generates internal stresses that lead to cracking and/or delamination of the concrete cover.

15.5.2 Carbon Dioxide

The carbonation of concrete consists of the reaction of carbon dioxide existing in the air with the calcium hydroxide resulting from hydration of the cement, with the formation of calcium carbonate. The phenomenon slowly modifies the physical and chemical properties of concrete. From a chemical point of view, these changes are characterized by a reduction in the hydroxide content in the concrete, leading to a marked decrease in the pH of the interstitial electrolyte to values lower than 10. As result, the passive film that protects the steel is not stable and the corrosion process begins, over the entire reinforcing steel surface. From a physical point of view, the formation of calcium carbonate is somewhat beneficial, since it has low solubility and is deposited in the concrete's pores, decreasing porosity and markedly

Fig. 15.21 Relative volume of iron corrosion products formed on the surface of reinforcements



increasing the resistivity of the medium. The carbonation rate depends on the rate of diffusion of carbon dioxide to the reinforcement–concrete interface, which is conditioned by the permeability of the concrete. The carbonation rate reaches a maximum for concrete humidity levels between 40 and 70 % [13].

15.5.3 Prevention/Remediation

The most appropriate method for preventing the corrosion of reinforcements should be chosen taking into account the location of the structure. In Portugal, LNEC specification E378 [14] defines different environmental exposure classes, according to the aggressive agent. This standard also establishes minimum binder dosages, the maximum water/cement ratio (w/c), and minimum cover thickness to be used according to environmental exposure classes. Dosage for cement varies from 260 to 360 kg of cement/m^3 of concrete, the maximum w/c ratio varies between 0.65 and 0.45, and minimum coating thicknesses are in the 20–45 mm range.

It is important to note that protection begins with the use of a good quality concrete, i.e., an appropriate content and type of cement, in order to ensure low permeability and high strength; with the choice of the correct cover thickness to protect the reinforcing steel; and with the choice of appropriate curing methods and processes to achieve the required concrete properties.

15.5.3.1 Monitoring

To measure the level of deterioration, to protect against corrosion or to prevent it from appearing, it is essential to carry out tests that make possible to assess the condition of the reinforcements. The following methods can be applied:

(a) Physical Methods

Visual inspection of the structure, taking photographs, identifying cracked and delaminated areas, determining the depth of reinforcements, taking X-rays and radiographic images, and removing holes, among others.

(b) Electrochemical Methods

Among the different electrochemical techniques that can be used to assess the level of reinforcing steel corrosion, the following stand out:

- *Measuring the open circuit potential of the reinforcement*—This technique makes possible to identify areas that are more susceptible to corrosion. Standard ASTM C-876-80 [15] related the electrode potential (referred to the Cu/CuSO$_4$ electrode) with the probability of corrosion, in accordance with the following criterion:

$E > -200$ mV	>95 % probability of corrosion not taking place
$E < -350$ mV	>95 % probability of corrosion taking place
-200 mV $< E < -350$ mV	≈50 % probability of corrosion taking place

  These values have, however, been criticized by many authors [16, 17] because the electrode potential depends on the conditions of the metal surface, specifically humidity levels and oxygen contents, among others, that mean the results must be interpreted carefully.

- *Measuring resistivity*—The probability of corrosion taking place depends on resistivity, according to Mays [18]:

Resistivity > 12 kΩ cm	Corrosion unlikely
Resistivity between 5 and 12 kΩ cm	Corrosion likely
Resistivity < 5 kΩ cm	Corrosion very likely

- *Measuring polarization resistance*—This technique is based on measuring the polarization resistance of a given section of the reinforcement, and this resistance is inversely proportional to the corrosion rate. This technique is easy to implement and some portable kits have been designed for application in situ.
- *Galvanostatic pulse*—Use of this technique for steel concrete systems has been defended by several authors [19] who justify it because it is an easily applied, fast technique that does not disturb the system and is based on simple theoretical background. Basically, the technique consists of the application of an instantaneous pulse of current to the reinforcing steel. The variation in electrochemical potential undergone by the system in the time between applications of the pulse is related to polarization resistance and makes it possible to calculate the corrosion rate.

15.5.3.2 Prevention Methods

The most common prevention methods include:

(a) *Coating of reinforcements with epoxy* (*nonmetallic*) *materials*—The coating should be applied correctly in order to guarantee good adherence to the concrete and to avoid the formation of fragile and delaminated areas that could become precursors for corrosion [20].

Fig. 15.22 Installation of a cathodic protection system in a structure during construction stage (courtesy of *ZetaCorr*)

(b) *Impregnating concrete with polymers*—This technique consists of impregnating the concrete with a monomer and polymerizing it in situ. A reduction in porosity is achieved as a result [21].

(c) *Galvanized steel*—The use of galvanized reinforcements is very common, although the galvanizing layer is unstable in very basic media, so the procedure does have some limitations.

(d) *Cathodic protection*—Cathodic protection is the most appropriate technique for protecting reinforced concrete structures, since it is able to reduce/prevent the corrosion process. This technique is extremely effective in protecting large structures. In Portugal, this technique is not widely used, although there are some recent examples of its use—Fig. 15.22.

(e) *Use of corrosion inhibitors*—Corrosion inhibitors are products that are added to the concrete mixture, so it is important to ensure that using them will not damage the rheological and mechanical properties of the concrete. In recent years, new generations of organic-based inhibitors have been developed, which migrate through the concrete and adsorb on the surface of the metal [22, 23], protecting the steel from the aggressive attack of chlorides.

(f) Use of stainless steel reinforcements—Stainless steel is much more resistive against localized and uniform corrosion attack. Therefore, when used as reinforcement, it is expected to resist for a longer time when compared to conventional cold rolled steel [24]. Various types of steel can be used, but 304 is the cheapest one.

(g) *Removing chlorides*—Electrochemically removal of chlorides involves applying a potential gradient between an external anode and the reinforcing steel, thereby forcing the chlorides to migrate to the outside of the concrete.

(h) *Re-alkalinization of concrete*—The objective of this technique is to reintroduce the alkaline content at the steel–concrete interface level. The technique is based on applying a potential gradient between an external anode and the reinforcement, which forces an alkaline agent (normally Na_2CO_3) to migrate to the concrete bulk, increasing the pH of the interstitial solution to values above 10.5, enough to ensure that the reinforcing steel remains in the passive condition.

References

1. Kich GH, Brongers MPH, Thompson NG (2002) Corrosion costs and preventive strategies in the United States. Mater Perform 41(7):16
2. Jones DA (1996) Principles and prevention of corrosion, 2nd edn. Prentice Hall, New York
3. Macdonald DD (1992) The Point Defect Model for the Passive State, J Electrochem Soc 139 (12):3434.
4. Pourbaix M (1974) Atlas of electrochemical equilibria in aqueous solutions, 2nd edn. NACE, Houston
5. During E (1981) Corrosion atlas. Elsevier, Amsterdam
6. Gentil V (1996) Corrosão, 3rd edn. LTC—Livros Técnicos e Científicos Editora S.A, Rio de Janeiro, Brazil
7. Panossian Z (1993) Corrosão e Protecção contra a Corrosão em Equipamentos e Estruturas Metálicas, vol 1. Instituto de Pesquisas Tecnológicas, São Paulo
8. Wranglen G (1972) An introduction to corrosion and protection of metals. Institut för Metallskydd, Stockholm
9. Fontana MG (1986) Corrosion engineering, 3rd edn. McGraw Hill, New York
10. Montemor MF, Simões AMP, Ferreira MGS (2003) Chloride-Induced Corrosion on Reinforcing Steel: From the Fundamentals to the Monitorisation, Cem Conc Comp 25:491.
11. Glass GK, Buenfeld NR (2000) The influence of chloride binding on the chloride induced corrosion risk in reinforced concrete, Corros Sci 42:329.
12. Glass GK, Reddy B, Buenfeld NR (2000) Corrosion inhibition in concrete arising from its acid neutralisation capacity, Corros Sci 42:1587.
13. Tuutti K (1982) Corrosion of steel in concrete. Swedish Cement and Concrete Research Institute, Stockholm, Sweden
14. MOPTC. Betões—Guia para utilização de Ligantes Hidráulicos. Especificação LNEC E378
15. ASTM C876 – 09, Standard Test Method for Corrosion Potentials of Uncoated Reinforcing Steel in Concrete
16. Montemor MF (1995) Estudo da Deterioracao por Corrosao de Estruturas de Betao Armado – PhD Thesis. Universidade Técnica de Lisboa, Instituto Superior Técnico, Lisbon

17. Montemor MF, Simões AMP, Ferreira MGS, Salta MM (2000) Effect of Fly ash on Concrete Reinforcement Corrosion Studied by EIS, Cem Conc Comp 22:175.
18. Mays G (ed) (1992) Durability of concrete structures. Chapman & Hall, London, UK
19. Elsener B, Wojtas H, Bohni H (1994) Galvanostatic pulse measurements – rapid on site corrosion monitoring, In: Swamy RN (ed) Proc. Intl. Conf. University of Sheffield. “Corrosion and Corrosion Protection of Steel in Concrete”, 24–28 July 1994, Sheffield, UK, p 236
20. Zoltanetzky Jr P, Gordon C, Faci PE, Parnes J (1994) New developments in corrosion inhibiting admixture systems for reinforced concrete, In: Swamy RN (ed) Proc. Intl. Conf. University of Sheffield. “Corrosion and Corrosion Protection of Steel in Concrete”, 24–28 July 1994, Sheffield, UK
21. Clear KC, Virmani YP (1982) Solving rebar corrosion problems in concrete. Preprint no. 4. NACE, Chicago
22. Jamil HE, Montemor MF, Boulif R, Shriri A, Ferreira MGS (2003) An electrochemical and analytical approach to the inhibition mechanism of an amino-alcohol-based corrosion inhibitor for reinforced concrete, Electrochim Acta 48(23): 3509
23. Jamil HE, Shriri A, Boulif R, Bastos AC, Montemor MF, Ferreira MGS (2004) Electrochemical behaviour of amino alcohol-based inhibitors used to control corrosion of reinforcing steel, Electrochim Acta 49(17–18):2753–2760.
24. Duarte RG, Castela AS, Neves R, Freire L, Montemor MF (2014) Corrosion Behavior of Stainless Steel Rebars Embedded in Concrete: an Electrochemical Impedance Spectroscopy Study, Electrochim Acta 124: 218–224

Structural Adhesives

16

João Custódio

Abstract

In recent years, there has been an increase in the use of adhesives in the construction sector. However, this growth is still limited by the lack of knowledge regarding the potential and limitations of this technology by designers, civil engineers and architects. This situation is due mainly to the fact that, in some countries, bonding technology is virtually absent from scientific literature, and because despite the vast number of international publications, the information available is very sparse and is not directed specifically to the construction sector. Thus, this chapter aims to contribute, in a succinct way, to the dissemination of the current state of knowledge regarding structural adhesives in the construction sector, as well as, to provide guidance concerning the bibliography that may be consulted by those who wish to study, in a greater depth, the various aspects of the thematic of structural adhesives.

Keywords

Adhesives • Adhesives classification • Adhesives characteristics • Structural adhesives • Adhesion • Adhesion theories • Bonded connection • Bonding system selection • Bonded connection design • Surface preparation • Durability • Process control

In recent years, there has been an increase in the use of adhesives in the construction sector. However, this growth is still limited by the lack of knowledge regarding the potential and limitations of this technology by designers, civil engineers and architects. This situation is due mainly to the fact that, in some countries, bonding

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M.C. Gonçalves, F. Margarido (eds.), *Materials for Construction and Civil Engineering*, DOI 10.1007/978-3-319-08236-3_16

technology is virtually absent from scientific literature, and because despite the vast number of international publications, the information available is very sparse and is not directed specifically to the construction sector. Thus, this chapter aims to contribute, in a succinct way, to the dissemination of the current state of knowledge regarding structural adhesives in the construction sector, as well as, to provide guidance concerning the bibliography that may be consulted by those who wish to study, in a greater depth, the various aspects of the thematic of structural adhesives.

16.1 Introduction

Adhesives have been used by man for thousands of years. However, adhesives were used for non-structural purposes and were of natural origin [1–3].

From the twentieth century onwards, natural adhesives began to be replaced by synthetic adhesives, with greater adhesion, superior possibilities of formulation, higher strength and durability. Nevertheless, adhesives of natural origin continue to dominate the market in some non-structural applications, given their lower cost and their greater environmental sustainability (since they are not derived from petroleum), being used, for example, in packaging for the food and pharmaceutical industries, on furniture and textile industries, and on all-purpose adhesives [1–3].

The era of structural bonding began in the twentieth century with the use of phenol-formaldehyde adhesives in structural plywood and glued-laminated timber inside buildings. The development of structural adhesives had a new and important impetus during World War II with its use in the manufacture of military aircrafts. The excellent weight/strength ratio that structural bonded connections exhibit has enabled the development of aircraft fuselages with good rigidity, strength, durability and low weight. Since then, the aviation industry has led the development of structural bonded connections, contributing in a preponderant way, not only for the development of synthetic structural adhesives and the understanding of the phenomena associated with adhesion but also for the optimisation of methods for the design, preparation and execution of bonded connections. The successful use of adhesives in that industry, renowned for its high level of demand with respect to safety and reliability, has increased the use of bonded connections. These have replaced traditional connection methods (such as screws, welding, brazing, rivets and other mechanical connections) with significant advantages. The success achieved by bonded connections in the aviation industry led to its expansion into other areas. Nowadays, they are present in almost all industrial sectors, e.g. shipbuilding, textiles, automobile, transport, furniture, packaging and construction [1–3].

Thanks to a significant progress during the last century, the science of adhesives and adhesion is sufficiently developed to allow the production of bonded structural connections, with high performance and excellent durability, in a wide variety of industries. Current developments are related, mainly, to perfecting existing formulations in order to optimise production costs, reducing environmental impact, adapting existing types of adhesives to new substrates (e.g. composite materials, ceramics) and new applications (e.g. bonding of composite concrete-timber structures, bonding of prestressed wood, reversible bonded joints) (Fig. 16.1).

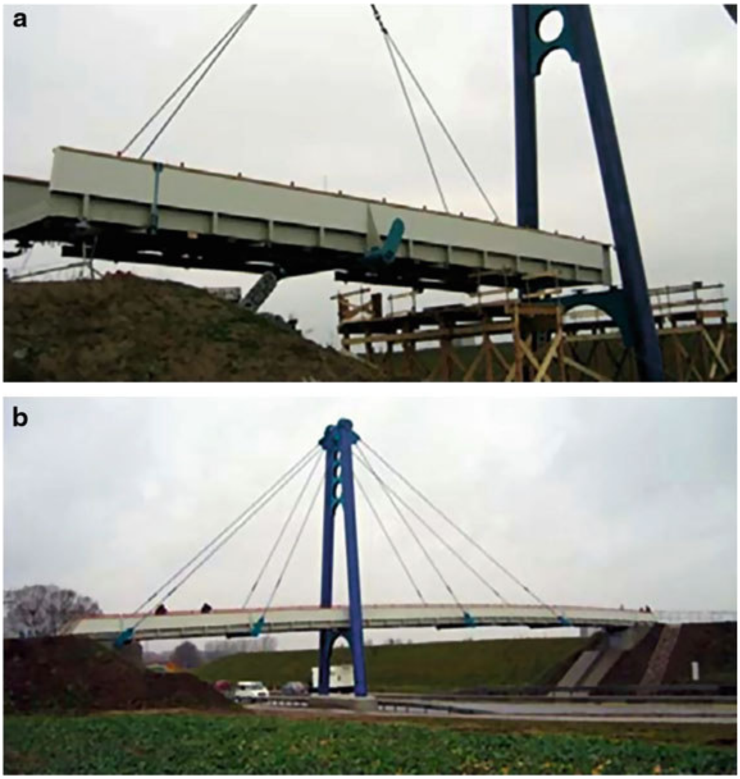

Fig. 16.1 Pedestrian Bridge in Schwerin, Germany. A two-component epoxy structural adhesive was used in this bridge to bond prefabricated elements of GFRP (glass fibre-reinforced polymer composite having an unsaturated polyester resin matrix) constituting the segments used in the bridge deck [4]

Although structural bonding is a well-established technique in some industries, it is still a relatively recent technology in the construction sector. For this reason, structural bonding is still approached with some caution by civil engineers. Also contributing to this situation is the fact that the use of structural bonding in civil engineering has some specific features compared with other industries. Notably, construction projects are generally unique and constructed in situ, rather than produced on a large scale and under controlled conditions, which leads to difficulties in choosing the type of solution adopted and the bonding agent to be used.

Among the various building materials, structural adhesives are most used in applications involving wood, mainly in the form of processed wood products such as wood-based panels and glued-laminated timber. Examples of applications include the use of wood-based panels for floors, walls and roof assemblies; wood-based panels together with solid timber or reconstituted solid wood products in beams, portals and roof frames; and glued-laminated timber in straight beams and

Fig. 16.2 Atlantic Pavilion. The roof structure of the Atlantic Pavilion was the first large glulam structure constructed in Portugal. The structure consists of 17 triangulated transversal arches with variable dimensions, having the largest arch 114 m in length and a maximum height of 47 m above the arena

in arches or portals with large span (Fig. 16.2). Adhesives also play an important structural role in fixing elements on the façades of buildings. Regarding concrete, the main uses are related with the joining of prefabricated concrete elements, fixing of anchorages and bonding fresh concrete to hardened concrete. An area of use in expansion is the use of adhesives in repairing and strengthening concrete or timber structures (Fig. 16.3). The use of bonded connections in metallic structures still has a very limited use. The use of adhesives with fibre-reinforced polymeric materials (a topic covered in detail in chapter "Polymer Matrix Composites") for the rehabilitation of concrete, steel, masonry and timber structures, among others, is another area that has endured great development over the past few years and experienced a significant increase of its use.

It is intended, in this chapter, to provide engineers and architects with basic knowledge that may allow them to better use adhesive products in the building sector. Thus, the fundamental aspects related to adhesion, the major characteristics of adhesives and bonded connections, the factors that influence performance and durability of bonded connections, as well as, the main techniques used to evaluate adhesives and bonded connections will be addressed.

This chapter will also briefly mention the main applications of these materials in the construction sector, as well as health, safety and quality control issues that must be taken into account when using them. Finally, future developments in this field will also be pointed out. Wherever possible, mention to the relevant normative documents for each application will be made.

16.1.1 Fundamental Definitions

Adhesive bonding technology acquired its own lexicon throughout its development. It is, thus, necessary to present the basic terminology used in this field, for the clear understanding of the phenomena related with this technology. Therefore, in the

Fig. 16.3 Use of structural adhesives in the repair and strengthening of timber structures (the images were kindly provided by Rotafix Ltd., more information concerning the work illustrated in the figures can be found in [5])

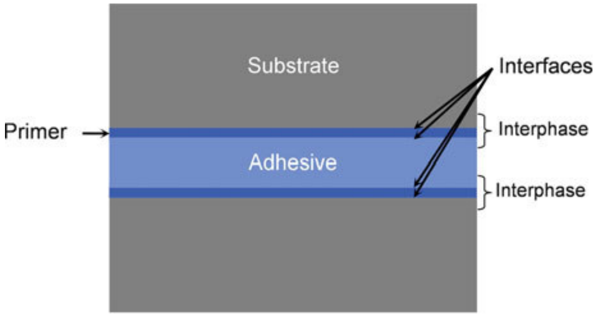

Fig. 16.4 Components of a bonded joint

following paragraphs, the most important terms will be defined. In addition, the reader will also be able to find the most relevant concepts presented throughout this chapter in the glossary, at the beginning of the book.

An adhesive is defined as a product that is able to maintain two surfaces belonging to one or more materials under a state of adhesion. Adhesion is defined as the phenomenon by which two surfaces are held together by chemical, physical or physico-chemical forces resulting from the presence of an adhesive.

The term adhesion is often confused with adherence, so it is important to clarify the differences between the two terms. While the first term refers to a phenomenon caused by an adhesive, the second term refers to a state in which two surfaces are held together by interfacial forces, with or without the presence of an adhesive. The term adherence is also often used to express quantitatively the adhesion produced by an adhesive, a less adequate use.

When one seeks to express the ability of a material to produce adhesion, the term adhesiveness should be used. The material (or surface of a material) which is bonded or is intended to be bonded to another material through an adhesive is defined as a substrate [6–9].

The bonded joint (Fig. 16.4) refers to the union of two adjacent substrates through an adhesive and therefore designates the assembly formed by the substrates, the adhesive, by any additional products that might be used (e.g. a primer) and all associated interphases. Unlike the term bonded joint, which refers to the site in which two surfaces are held together by the adhesive, the term bonded connection is used more broadly to describe a structural element resulting from the bonded joint. The primer is the coating that sometimes is applied to a substrate prior to bonding, in order to improve adhesion and/or durability of a bonded joint. The region of finite dimension, extending from the zone where local (chemical, physical, mechanical and morphological) properties of the substrate begin to differ from those that it has as a bulk material (i.e. in the internal regions of the material, away from the interface) to the area where the local properties are the same as the ones that the adhesive has as a bulk material, is called interphase. The nature of the interphase is a critical factor in the properties and quality of the bonding.

The interface is defined as the contact face between the surfaces of two materials, and, as such, is contained in the interphase [6–9].

Bonded connections can be classified into three categories, namely, structural, non-structural and semi-structural. In structural bonded connections, a connection must bear the service load and/or limit loads in a specific direction. The rupture of such connections results in significant changes in the behaviour of the structure and/or its ability to withstand the loads for which it was dimensioned, which may lead to a structural failure. In semi-structural bonded connections, the bond only has to distribute the stresses applied, since there is another system in the structure that is responsible for withstanding the loads. The rupture of such connections may result in changes in the load-bearing capacity, but it does not affect its ability to withstand limit loads. In non-structural bonded connections, the bond is subject only to individual tensions; therefore, the consequences of the bond's failure are negligible for the structure, although they may cause injury to the occupants of the structure.

This chapter will address only structural and semi-structural connections. It is important to note that since these are general categories, it may not be obvious in which category some applications of these systems fit in. For example, there may be situations where the connection uses the bonded joint to withstand shear stresses, but uses other systems to withstand peel or cleavage stresses.

Finally, it is important to distinguish between those situations where the adhesive is an integral part of the structural material, as in the case of glued-laminated timber, and those where the adhesive is used for bonding structural elements. In the first case, the choice of the type of adhesive is made by the material's manufacturer. The engineer only needs to consider the connection's design and detailing, having into account the strength of the material, and not addressing the adhesive's behaviour in service. In the second case, the engineer needs not only to consider the design and detailing of the connection but also to specify the adhesive's strength characteristics. Thus, it is advisable for the engineer to consult experts in adhesives before taking any decisions.

16.1.2 Advantages and Disadvantages of Using Adhesives

The main advantages and disadvantages associated with the use of structural bonded connections are listed below [2, 3, 10–13]. The order in which they are presented is not related to the relative importance of each one, since the relevance of each factor varies according to the particular application in which they are used, and in some cases, certain factors may even not be relevant.

16.1.2.1 Advantages

- *Weight reduction:* adhesives have an excellent weight/strength ratio in comparison with mechanical alternatives and, therefore, are normally used in small amounts, thus contributing not very significantly to the weight increase of the connection. Consequently, comparing bonded connections to traditional connections using mechanical fasteners, the former present lower weight.

- *No damage to the substrate:* applying adhesive does not damage the substrate and it retains its mechanical properties intact, unlike the case with most traditional mechanically fastened connections. For example, the use of rivets or screws involves drilling a hole in the substrate, which will give rise to stress concentration on this area and can cause a reduction in the physical properties of the substrate and the mechanical properties of the connection.
- *Greater use of the substrate's strength:* when bonded connections are correctly designed and executed, no stress concentrations are present in the joint, and therefore the properties of the substrate can be fully used.
- *Good fatigue resistance:* adhesives are polymeric materials that exhibit viscoelastic properties, which allows them to absorb mechanical energy applied to the bonded joint, in the form of shocks or vibrations, and dissipate it as heat. For this reason, bonded connections are usually more resistant to fatigue than traditional mechanically fastened connections.
- *Connecting thin and/or fragile substrates:* applying adhesives does not involve the application of mechanical energy and, therefore, adhesives can be used to join brittle materials. In addition, since they are polymeric materials, they have lower strength than that presented by mechanical fasteners and, hence, adhesives will not contribute to the deterioration of thin substrates.
- *Invisibility:* bonded connections are, in most cases, invisible.
- *Joint sealing:* adhesives allow a connection to be formed and sealed in just one step.
- *Good corrosion resistance:* adhesives are immune to corrosion and, as most are neither ionic nor conductive, bonded connections allow for the bonding of metals that would suffer from galvanic corrosion if connected otherwise.
- *High and uniform rigidity:* bonded connections possess a high effective rigidity, whereas in connections with screws there may be some slippage. Bonded connections also have a high and uniform rigidity throughout the bonded joint; this allows the transfer of high loads more efficiently.
- *Better stress distribution:* bonded joints allow distributing applied stresses in a more uniform manner throughout the bonding area. This area is always greater than the solicited area when using mechanical connectors, which gives the bonded joint greater rigidity and a higher load transmission capacity, reducing weight and cost and increasing fatigue resistance.
- *Joining different materials:* adhesives have excellent ability to bond materials with composition, expansion coefficient, thermal conductivity, strength and other different properties (metals, rubbers, plastics, foams, fabrics, wood, ceramics, glass, etc.), and an excellent ability to join temperature-sensitive materials (thermoplastic, magnetic materials, etc.).
- *Vibration reduction:* bonded connections have a good capacity of absorbing vibrations and noise due to their viscoelastic properties.
- *Versatility:* bonded joints allow the effective joining of materials with any given thickness and geometry, making the design more flexible and allowing the use of new materials and concepts.

- *Fastness:* generally, bonded connections involve the use of fewer components and therefore have the potential for a simpler and faster manufacturing process than mechanically fastened connections, which can also provide economic benefits.

16.1.2.2 Disadvantages

- *Localised stresses and peel and cleavage forces:* it is necessary that the bonded connection is designed to eliminate, as much as possible, the peel and cleavage forces and localised stresses. The best solution is to conceive a connection where the adhesive is subject only to shear tensions.
- *Surface preparation:* bonded connections are based on the phenomenon of adhesion to transfer the load. As the phenomenon of adhesion is manifested on the surface of the substrate, the condition of the latter strongly influences the strength of the bonded joint, hence the need to properly prepare the surfaces to be bonded.
- *Knowledge:* less knowledge and experience in the use of this technology in comparison with traditional mechanically fastened connections.
- *Variability of adhesive products:* properties of adhesive products vary significantly between manufacturers and are constantly evolving.
- *Strict control of the process:* the need to use trained personnel, to perform a strict control of the preparation and application of the adhesive products and to implement a quality control plan.
- *Curing conditions:* in general, adhesive products require controlled environmental conditions during application and curing, which can be difficult to achieve in some in situ applications.
- *Toxicity and flammability:* the use of adhesive products may have implications in terms of health and safety, as components of adhesives can be toxic and/or flammable, although the same risks can be found in some types of mechanical connections, such as welding.
- *Duration of curing:* the waiting time required for the bonded joint to acquire the total load-bearing capacity may be higher than the time required to apply screws, welding or other mechanical fasteners. However, as the installation of bonded connections involves, in general, less complex operations, this phase may be faster, so that the total duration of the operation is usually equal to or less than that achieved with mechanical fasteners.
- *Inspection:* in general, mechanical fastenings are applied in the exterior of structural element and, therefore, they are easily visible and inspectable. By contrast, in most cases adhesive connections are implemented inside the structural element, so that they are more difficult to inspect, when completed and during their lifetime.
- *Dimensions:* adhesive connections have limited resistance to certain load directions, so that their correct design is vital to obtain an adhesive connection with a performance and durability adequate for the specific application.
- *Limited reversibility:* adhesive connections cannot be dismantled, even though they can, in most cases, be removed without sacrificing too much substrate.

- *Limited performance and strength in severe or extreme conditions:* the properties of the adhesives are affected by the environment (e.g. temperature and humidity) and extreme conditions (e.g. fire).
- *Creep:* can be a problem, especially in situations of continuous and prolonged exposure to high temperatures.
- *Fragility:* some adhesive products are brittle, especially at very low temperatures.
- *Durability:* since it is a relatively new technology, the long-term performance of bonded connections, especially in adverse conditions, is often uncertain.
- *Regulatory framework:* for most applications, there is no adequate regulation regarding the design and detailing of the adhesive connections and regarding the specification of adhesive products and techniques to be used in the interventions.
- *Inspection/maintenance:* lack of non-destructive inspection techniques for evaluating the condition of bonded connections, both initially and during the service life of the connection.

As can be inferred from the advantages and disadvantages mentioned, there might be cases in which it is more appropriate to use traditional methods of mechanically fastened connections or even a combination of both. It should be noted that in situations where the connection uses mechanical fasteners and adhesives, the final strength of the connection is not equivalent to the direct sum of their individual strength, although the combined ultimate strength may be higher. The combined use of adhesives and mechanical connectors can be useful in cases where the connection is subject to loads in different directions. For example, shear forces may be supported by the adhesive, and normal stresses, that would tend to open the bonded joint, may be supported by mechanical fasteners. The use of combined connections may not be recommended in situations where it is necessary to have a rigid bond operating at high temperatures, since the adhesive can suffer a decrease in its strength and thus making the bond less rigid. On the other hand, the use of a combined connection may make it more rigid than the connections in its vicinity and thereby attract more load for that connection and to the adjacent ones, resulting in a change of the overall behaviour of the structure, and possibly creating problems elsewhere. The decision as to which joining method to use should be made as early as possible in the process of obtaining the connection, since it will constrain its geometry, the construction methodology of the work and, therefore, the final cost [2, 3, 10–13].

Fire resistance of bonded connections may be higher or lower than the traditional methods of mechanically fastened connections depending on the application in which they are used. For example, when the product is used for bonding inside the structural element, and the alternative mechanical fastening method is applied outside of the structural element, there may in fact be advantages in the adhesive bonding. However, if the adopted solution involves bonding in the exterior of the structural element, its fire resistance is most likely lower than that achieved by a mechanically fastened connection.

16.2 Adhesives

16.2.1 Classification

Adhesives can be classified in several ways, namely according to their origin, chemical composition, field of application, physical form, mode of curing/setting, mode of application, material to bond, application environment, cost, etc.

16.2.1.1 Origin

The classification of adhesives according to their origin divides them as being from *natural* or *synthetic* origin. Natural origin adhesives can be divided into three types: vegetable, animal and mineral (Table 16.1). Synthetic adhesives include all the remaining.

16.2.1.2 Chemical Composition

The classification of adhesives based on their chemical composition divides them into four categories: *thermoplastic, thermosetting, elastomeric and hybrid* (Tables 16.2 and 16.3). These categories are, in turn, subdivided into families, such as epoxy and phenolic.

The main characteristic of thermoplastic adhesives is that they do not cure (process of developing resistance properties through a chemical reaction, of cross-linking and/or polymerisation) and do not set (the process by which the forces of cohesion and/or adhesion are chemically or physically developed, e.g. polymerisation and oxidation) with the application of heat. Since these adhesives do not develop a cross-linked polymeric structure (the polymeric structure in which the polymer chains are connected to each other through multiple intermolecular covalent or ionic bonds), they can be melted and applied to a substrate. Once the bonded joint is formed, the hardening of the adhesive takes place by cooling or evaporation of water or solvents. While these adhesives can be repeatedly melted and hardened, the repeated exposure to the high temperature required for their melting may cause their deterioration, which limits the number of thermal cycles that they may be subject. Thermoplastic adhesives are less resistant to temperature, moisture and solvents than thermosetting adhesives. Although some thermoplastic adhesives can provide excellent resistance to shear stresses at moderate temperatures, the fact that they do not have a cross-linked polymeric structure makes them susceptible to creep, even at low temperatures. In most situations it is this characteristic that prevents them from being used as structural adhesives [2, 3, 10, 12, 22].

Thermosetting adhesives are characterised by undergoing a process of irreversible curing at room or elevated temperatures with or without the application of pressure, depending on the type of adhesive, and thus develop a cross-linked polymeric structure, which is substantially infusible and insoluble. Due to their highly cross-linked polymer structure, thermosetting adhesives are highly resistant to heat, humidity and solvents, with minimal elastic deformation under the action of loads. For this reason, most of the structural adhesives are thermosetting in nature.

Table 16.1 Main natural origin adhesives [2, 3, 10, 12, 14–24]

Origin	Type	Family	Examples
Natural	Animal	Proteins	Albumin (egg white—ovalbumin; milk—lactalbumin; blood—seralbumin)
			Collagen (remains of animals—bone, skin, cartilage, tendons, etc.)
		Phosphoproteins	Casein, CS (milk)
		Resins	Shellac
		Waxes	Beeswax
	Vegetable	Resins	Rosin (colophony)
			Canada balsam
			Natural rubber (isoprene rubber), NR
			Copal
			Dammar
			Mastic
			Sandarac
		Oils and waxes	Linseed oil
			Carnauba wax
		Proteins	Leguminous plants (soy, pea, peanut)
			Cotton
			Colza or canola
		Polysaccharide	Plant gum exudates (arabic, ghatti, karaya, tragacanth)
			Seed gums (guar, carob, tamarind)
			Plant extracts (arabinogalactan; agar-agar and algin or alginate, derived from algae)
			Xanthan and dextran
			Starch
	Mineral	Inorganic minerals	Silicates
			Phosphates
			Magnesium, lead and sulphur compounds
		Mineral waxes	Paraffin
		Mineral resins	Amber
		Bitumen	Asphalt
			Bitumen
			Tar

Note: Although paraffin is an organic material, its adhesive is usually classified as of mineral origin [14]

Elastomeric adhesives are based on natural or synthetic elastomers and possess a low elasticity modulus, a high tenacity and a large capacity of elongation. These adhesives are able to deform considerably when stretched or compressed, resuming the initial size and shape once the load is removed. As a result, their bonded connections can absorb much energy and have a considerable resistance when subjected to uneven loads. These adhesives can be thermoplastic or thermosetting.

Table 16.2 Main synthetic origin adhesives [2, 3, 10, 12, 14–19, 21–23]

Origin	Type	Family	Examples
Synthetic	Elastomeric	Rubber	Polysiloxane (silicone), SI*
			Poly(styrene-butadiene), SB*
			Poly(styrene-acrylonitrile), SAN*
			Poly(acrylonitrile-butadiene), AB*
			Poly(acrylonitrile-butadiene-styrene), ABS*
			Polybutadiene, PBD*
			Polyisobutylene, PIB*
			Polychloroprene (or Neoprene), CR**
			Polyisoprene, PIP or IR**
			Polysulfide, T or TR**
	Thermoplastic	Cellulose derivatives	Cellulose acetate, CA*
			Cellulose acetate butyrate, CAB*
			Cellulose caprate
			Cellulose nitrate, CN*
			Methyl cellulose, MC*
			Hydroxyethyl cellulose, HEC**
			Ethyl cellulose, EC*
			Carboxymethyl cellulose, CMC*
		Polyvinyl	Ethylene-vinyl acetate copolymer, EVAC*
			Poly(vinyl alcohol), PVAL*
			Poly(vinyl acetate), PVAC*
			Poly(vinylidene dichloride), PVDC*
			Poly(vinyl butyral), PVB*
			Poly(N-vinylpyrrolidone), PVP*
		Saturated polyesters	Polystyrene, PS*
			Polyamide, PA*
		Polyacrylates	Polyacrylate, PAK*
			Polymethacrylates [poly(methyl methacrylate), PMMA; poly(ethyl methacrylate), PEMA; poly (butyl methacrylate), PBMA]*
		Polyethers	Polyhydroxy ether
			Polyphenolic ether
		Polysulfones	Polysulfone, PSU*
			Poly(phenylene sulfone), PPSU*
	Thermoset	Aminoplastic	Urea-formaldehyde, UF*
			Melamine-formaldehyde, MF*
			Melamine-urea-formaldehyde, MUF*
		Epoxy	EP
		Phenolic	Phenol-formaldehyde, PF*
			Resorcinol-formaldehyde, RF
			Phenol-resorcinol-formaldehyde, PRF

(continued)

Table 16.2 (continued)

Origin	Type	Family	Examples
		Unsaturated polyesters	UP*
		Polyaromatics	Polyimide, PI*
			Polyphenylene
			Polybenzimidazole, PBI**
			Bismaleimide, BMI
		Isocyanates	Polyurethane, PUR*
			Methylene diphenyl diisocyanate, MDI**
			Toluene diisocyanate, TDI**
		Cyanoacrylate	Poly(methyl cyanoacrylate)
			Poly(ethyl cyanoacrylate)
		Furans	Furan-formaldehyde, FF*
			Poly (phenol-furfural)

Note: The examples given present the common assigning to a family and to a type of adhesive, however, it is possible that some adhesives (e.g. polyaromatics, polyurethane) have formulations that assigns them to a family and type of adhesive different than the one presented. The abbreviations used generally follow the nomenclature defined in [25] when marked with * in all other cases, when marked with **, the common nomenclature is followed, as defined on [26] and [27]

Table 16.3 Main hybrid adhesives [2, 3, 10, 12, 14–19, 21–23]

Origin	Type	Family	Examples
Natural/synthetic	Hybrid	Epoxies modified with	Rubber
			Phenolic resins
			Aminoplastic resins
			Polyamides
			Polysulfides
			Polymers and copolymers of vinyl
		Phenolics modified with	Nitriles
			Polymers and copolymers of vinyl
			Polychloroprene

Due to their highly viscoelastic nature, elastomeric adhesives exhibit good resistance to peel forces. These features allow them to be used for bonding substrates with different coefficients of thermal expansion, to dampen vibrations and absorb sound waves [2, 3, 10, 12, 22].

Hybrid adhesives are manufactured by combining thermoplastic, thermosetting or elastomeric resins, in a single formulation, in order to take advantage of the most important properties of each component. This type of adhesive is normally used in very demanding applications where its high cost is acceptable, as in the military applications, the aerospace and the transportation industry [2, 3, 10, 12, 22].

16.2.1.3 Field of Application

The classification of greater practical interest is that which relates to the field of application. The distinction is made between *structural*, *semi-structural* and *non-structural* adhesives. Table 16.4 presents the principal adhesives used in construction, grouped according to this classification.

There are several definitions for a structural adhesive. It can be defined as an adhesive that forms a bonded joint capable of sustaining a specified load on a structure for a defined long period of time [9]; as an adhesive with proven reliability in structural applications and that produces bonded joints capable of being stressed to a high proportion of its maximum failing load for long periods without failure [28]; or even as an adhesive which allows to transfer loads between the adherends in a bonded joint exposed to typical environmental service conditions of the structure on which it is applied [7]. Regardless of the adopted definition, the group includes all of the adhesives capable of producing bonds that have a shear strength greater than 4–10 MPa and a performance and durability such as to enable them to maintain the integrity of the bonded connection, when exposed to the expected service conditions over the entire service life of the structure.

While a structural adhesive contributes to the strength and to the rigidity of the structure, a semi-structural adhesive only contributes to its rigidity. Additionally,

Table 16.4 Adhesives usually chosen for each type of application [3, 10, 14, 21–23]

Application	Adhesive
Structural	Aminoplastic
	Epoxy, EP
	Hybrid epoxy
	Phenolic
	Hybrid phenolic
	Polyurethane, PUR (thermosetting)
	Isocyanates
	Polyaromatic
	Modified acrylic
	Cyanoacrylate
	Casein, CS
Semi-structural	Polyurethane, PUR
	Poly (vinyl acetate) cross-linked, PVAC-R
	Polyesters (unsaturated), UP
Non-structural	Animal adhesives (proteins, resins and waxes)
	Vegetable adhesives (resins, oils, waxes, proteins and polysaccharides)
	Mineral adhesives
	Elastomeric adhesives
	Thermoplastic adhesives

Note: This table presents the most common assigning of each adhesive or family of adhesives to a type of application. However, it is possible that some adhesive presented, or that some adhesives within the presented family have a particular formulation that allows them to be used in a different application field of the above presented

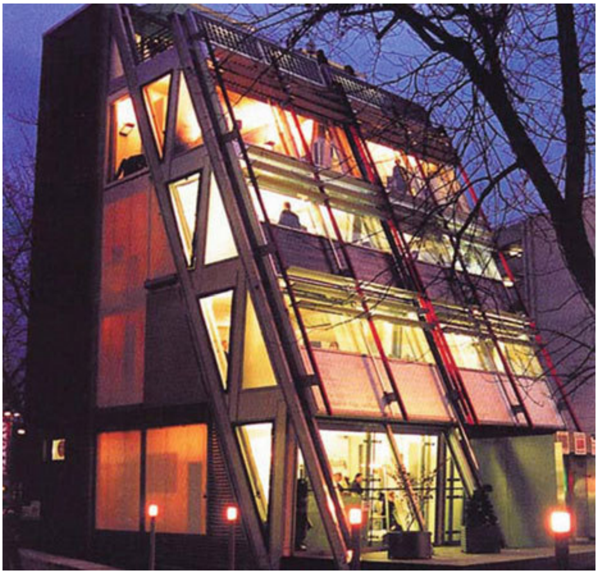

Fig. 16.5 Eyecatcher Building [4]

the bonded connections produced by these adhesives are not able to withstand without presenting deformation, the applied loads for extended periods.

Non-structural adhesives are used in situations that require low or moderate strength, in which their function is to hold lightweight materials in place. They are also used to produce secondary or temporary connections (with mechanical connections, in order to decrease their number and allow the improvement of properties such as vibration damping and joint sealing or acoustic insulation). These adhesives creep under moderate loads and generally degrade after prolonged exposure to the environment.

Figure 16.5 shows an example of the application of bonded connections in mobile structures. The Eyecatcher Building is currently the tallest building in the world to use a composite material structure. The mobile building of five floors has a height of 15 m and a base with an area of $10 \times 12\ \text{m}^2$. The supporting structure of the building comprises three parallel trapezoidal frames consisting of GFRP pultruded profiles (composite matrix material isophthalic polyester reinforced with glass fibres) bonded together with a two-component epoxy adhesive. In this building the primary structural connections are ensured by mechanical connectors to facilitate the assembly and disassembly of the structure [4].

16.2.1.4 Physical Form and Type of Curing/Setting

Adhesives can also be classified according to the physical form in which they are applied or sold, being the most common of these, liquid, paste, grout, aerosol, powder, tape, film, etc. They can also be classified according to the way they develop their strength properties. Adhesives may harden by chemical reactions (polymerisation and/or cross-linking promoted by reaction with hardeners, catalysts or by exposure to an external energy source—heat, radiation, etc.), by diffusion or evaporation of water or solvent or by cooling from a molten state [2, 3, 10, 12, 22].

The adhesives that harden by chemical reaction include two-component systems; single-component adhesives that cure under the action of a catalyst or hardener; adhesives that cure in the presence of moisture; adhesives which cure under the action of radiation (visible, ultraviolet, radio frequency, etc.); and adhesives that are catalysed by the substrate and adhesives in solid form (tape, film, powder, etc.). The reactive adhesives more used in structural and semi-structural applications are epoxy, polyurethanes, modified acrylic and cyanoacrylates [2, 3, 10, 12, 22].

The adhesives that harden by solvent or water loss include contact adhesives, pressure-sensitive adhesives, reactivatable adhesives and resinous solvent adhesives. These and the adhesives which harden upon cooling from a molten state are mainly used in non-structural applications [2, 3, 10, 12, 22].

The type of curing can be a very important factor when choosing the adhesive to use for a given application, as it may condition the properties of the adhesive that will be obtained. For example, if the application in question requires that curing is done at ambient temperature, the adhesive properties at high temperatures might be lower than desired, since for some adhesives a cure at ambient temperature does not enable a very high cross-linking level.

16.2.1.5 Substrate and Type of Environment

Adhesives can also be generically classified according to the material to bond or the service conditions where they are used. Thus, adhesives can be classified according to the type of substrate for which they are best adapted, for example, as adhesive for masonry, wood, concrete, metal, plastic, ceramic, etc., or according to the type of environment or service conditions in which they will be used, e.g. as adhesives resistant to acids, heat, environment, oils, etc.

16.2.1.6 Durability

Given the influence that the water content has in the mechanical properties of wood and wood derivatives, Eurocode 5 (EC5) [29] defined three types of situations that characterise the aspects of mechanical degradation risk of wood products, assigned by service classes. Environmental conditions (temperature and relative humidity) that correspond to each class and the corresponding type of environment are shown in Table 16.5.

When adhesives are used in timber structures, these service classes allow classifying adhesives according to durability presented in specific climatic conditions, facilitating the process of selecting an adhesive for a given application. In the particular case of structural aminoplastic or phenolic adhesives, two types of adhesives have been defined, namely I and II, to allow their assignment to the service classes mentioned above [30]. Generally, Type I adhesives can be used in service classes 1, 2 and 3, while Type II adhesives can be used in service class 1 only.

Table 16.5 Service classes defined in Eurocode 5 for wood structures (adapted from [29])

Service classes		End use	Moisture content in the wood
1	Climatic conditions characterised by a moisture content in the materials corresponding to a temperature of 20 °C and the relative humidity of the surrounding air only exceeding 65 % for a few weeks per year	Indoors with ventilation and heating. No risk of wetting in service	≤12 %
2	Climatic conditions characterised by a moisture content in the materials corresponding to a temperature of 20 °C and the relative humidity of the surrounding air only exceeding 85 % for a few weeks per year	Indoors without ventilation and heating. Sheltered outdoor environments. Risk of occasional wetting in service	≤20 %
3	Characterised by climatic conditions leading to higher moisture contents than in service class 2	Non-sheltered outdoor environments. Environments where there is an exposure to moisture areas. Risk of frequent wetting in service	>20 %

Note: The indicated values of moisture content in wood correspond to the equilibrium moisture content for solid softwoods

In the case of wood structures, the classification of the adhesives according to the service conditions in which they may be used can also be related to their functional classification. Table 16.6 features the most common adhesives grouped by application type and service conditions and classified as being used outdoors (without limitations), outdoor protected from direct action of atmospheric elements and indoors.

16.2.1.7 Cost

Cost is not usually used as a method of classification for adhesives. However, it is an important factor in the selection of an adhesive for a particular application, and therefore an indirect method of classification. When the cost associated with the use of an adhesive is estimated, it must be considered not only the price of the adhesive itself but also all the costs associated with implementation, namely, the cost of hand labour and equipment, the curing time of the adhesive, the losses resulting from application errors, the elimination of waste and the costs related to quality control.

16.2.1.8 Additional Classifications

In addition to the classification methods listed in this section, there are still many others (based on mode of application of the adhesive—spray, brush, spatula, syringes, caulking gun, etc.; on the adhesive broad chemical family and on the properties of the adhesive (e.g. shear strength and viscosity) - ASTM D4800 [31], etc.); but, due to their low popularity, they are not described here, except for the method proposed in the standard ASTM C881/881 M [32]. The classification described in this standard

Table 16.6 Adhesives usually chosen for each type of service conditions [23]

Application	Service conditions	Type of adhesive
Structural	Outdoors (Service classes 1, 2 and 3)	Phenol-formaldehyde, PF
		Resorcinol-formaldehyde, RF
		Phenol-resorcinol-formaldehyde, PRF
		Emulsion polymeric diphenylmethane diisocyanate, eMDI
		Melamine-formaldehyde, MF
	Protected outdoors (Service classes 1, and 2)	Melamine-urea-formaldehyde, MUF
		Polymeric diphenylmethane diisocyanate, pMDI
		Epoxy, EP
		Polyurethane, PUR (thermosetting)
		Modified acrylic
	Indoors	Urea-formaldehyde, UF
		Blood
		Casein, CS
Semi-structural	Protected outdoors (Service classes 1 and 2)	Polyurethane, PUR
		Poly(vinyl acetate) cross-linked, PVAC-R
		Polyesters (unsaturated), UP
Non-structural	Indoors	Animal adhesives
		Elastomers
		Poly(ethylene-vinyl acetate), EVA
		Polyesters (saturated), SP
		Poly(vinyl alcohol), PVAL
		Poly(vinyl acetate), PVAC
		Soy
		Starch

Note: This table shows the most common assignment of each adhesive to a category of use, but it is possible that an adhesive with a specific formulation cannot be used in the application and conditions of service presented or might be used in a different category from that shown

was developed with the aim of providing a method of classification of universal application for two-component epoxy-resin bonding systems for Portland cement concrete bonding and, at the same time, providing a system that allows the specification of adhesives based on their characteristics (e.g. bond strength, heat deflection temperature, compressive strength, compressive modulus, tensile strength). With this system, a bonding system can be classified by type, grade, class and colour.

In this classification seven types of bonding systems are defined, based on physical requirements: *Type I—used in non-structural applications to bond hardened concrete to hardened concrete or other materials, and as a binder in epoxy mortars/concretes; Type II—used in non-structural applications to bond fresh concrete to hardened concrete; Type III—used to bond skid-resistant materials to hardened concrete and as a binder in epoxy mortars/concretes used on traffic-bearing surfaces (or surfaces subject to thermal or mechanical movements); Type IV—used in structural applications to bond hardened concrete to hardened* *concrete or other materials, and as a binder in epoxy mortars/concretes; Type V—used in structural applications to bond fresh concrete to hardened concrete; Type VI—used to bond and seal segmental precast elements, and for span-by-span erection when temporary post-tensioning is applied; and Type VII—used as non-stress carrying sealer for segmental precast elements when temporary post-tensioning is not applied* [32]. *The specific physical requirements of the adhesives for each type of bonding system are detailed in the standard.*

This classification subdivides the bonding systems in three grades according to its flow characteristics, namely: *Grade I—low viscosity; Grade II—medium viscosity; and Grade III—non-sagging consistency* [32].

This classification subdivides the various types of bonding systems as defined above, into six classes according to the temperature of the surface of the hardened concrete substrate in which the bonding system is to be applied (it must be noted that this temperature may differ considerably from the ambient temperature) as follows: *Class A—used for temperatures below 4 °C; Class B—used for temperatures between 4 ° C and 15 ° C; Class C—used for temperatures above 15 °C; Class D—used for temperatures between 4 ° C and 18 ° C; Class E—used for temperatures between 15 ° C and 30 ° C; and Class F- used for temperatures above 25 ° C*. Classes A, B and C are valid for bonding systems of types I, II, III, IV and V. Classes D, E and F are valid for bonding systems of types VI and VII. For Class A, the manufacturer of the product shall define the lowest allowable temperature. For Classes C and F, the manufacturer of the product shall define the highest allowable temperature [32].

Finally, this classification subdivides the bonding systems according to their colour. The two-component epoxy systems are usually sold without any pigmentation, but, for some products, the purchaser may ask the manufacturer for the supply of coloured or darkened systems. Consequently, when ordering a bonding system, the purchaser shall specify the type, grade, class and colour of the bonding system desired.

16.2.2 Characteristics

The following tables briefly present the main characteristics of adhesives commonly used in structural and semi-structural applications (Tables 16.7, 16.8, 16.9, and 16.10).

Table 16.7 Overview of adhesives used for structural applications [3, 14, 23, 33–40]

Adhesive	Characteristics	Use
PF	High dry and wet strength; very resistant to water and humidity; more resistant than wood to high temperatures and chemicals	Glulam, PW for exteriors, HB, OSB and WB (softwoods)
RF	High dry and wet strength; very resistant to water and humidity; more resistant than wood to high temperatures and chemicals. Gap-filling properties. Adequate for difficult bonding conditions. It should not be used to bond directly to metals	Glulam, PSL, LVL, bonded joints exposed to severe conditions, components of boats, outdoors furniture, fire-rated panels
PRF		Bridges, piers, glulam, PW and fibreboard
eMDI	High dry and wet strength; very resistant to water and humidity; very resistant to prolonged and repeated periods of wetting and drying; resistant to high temperatures. Adheres well to metals and plastics	Glulam, flakeboard, OSB, bonding PW to steel and plastic, doors, decorative/ architectural materials
MF	High dry and wet strength; very resistant to water and humidity; resistant to high temperatures	Glulam, PW and P for exteriors (hardwoods), finger joints

Note: *Glulam* glued-laminated timber, *HB* hardboard, *LVL* laminated veneer lumber, *OSB* oriented strand board, *P* particleboard, *PSL* parallel strand lumber, *PW* plywood, *WB* waferboard

Table 16.8 Overview of adhesives used for structural applications [3, 14, 23, 33–40]

Adhesive	Characteristics	Use
MUF	High dry and wet strength; resistant to water and with a moderate resistance to humidity and temperatures up to 50 ºC	PW decorative (hardwoods), joining PW (softwood), bonding of wood veneers and lamellas
pMDI	High dry and wet strength; very resistant to water and humidity; very resistant to prolonged and repeated periods of wetting and drying	OSB, WB, P
EP	Extremely versatile; multiplicity of formulations; excellent shear strength; poor peel strength; high dry and wet strength; excellent adhesion to wood, metal, glass, ceramics and plastic; excellent resistance to moisture and chemical products; good gap-filling properties. Their bond lines delaminate when exposed to cycles of high humidity and high temperature	Widely used in the repair and strengthening of timber, glulam, steel, masonry or concrete structures. Bonding of wood veneers and lamellas without application of heat. Bonding of boats and aircraft components. Repair of structural and decorative elements
Modified acrylic	Good durability; fast cure; can be used as a primer; moderate cold resistance; less brittle than EP; some formulations have high peel strength and impact resistance; depending on the formulation can be used to fill voids	Excellent adhesion to concrete, metal, wood, plastics and composites. Some formulations can be used in outdoor structural applications

Note: *Glulam* glued-laminated timber, *HB* hardboard, *LVL* laminated veneer lumber, *OSB* oriented strand board, *P* particleboard, *PSL* parallel strand lumber, *PW* plywood, *WB* waferboard

Table 16.9 Overview of adhesives used for structural applications (continued) [3, 14, 23, 33–40]

Adhesive	Characteristics	Use
UF	High dry strength; moderate resistance to water, humidity and temperatures up to 50 ºC. Can emit formaldehyde when in service	Hardwood flooring, hardwood PW (decorative), PB, fibreboards. Bonding of wood veneers and lamellas and PVC to PW, MDF and P
Blood	High dry strength; moderate resistance to water, humidity and microorganisms	Softwood PW (indoors). Sometimes used in combination with soybean adhesive. Almost entirely replaced by phenolic adhesives
Casein	High dry strength; moderate resistance to water, humidity and moderated temperatures	Doors, PW not exposed to high humidity. No longer used for bonding wood lamellas. Replaced by phenolic adhesives

Note: *MDF* medium density fibreboard, *P* particleboard, *PVC* poly(vinyl chloride), *PW* plywood

Table 16.10 Overview of adhesives used for structural and semi-structural applications [3, 14, 23, 33–40]

Adhesive	Characteristics	Use
CA	Very fast cure; good adhesion to many materials without application of heat and with very thin bond lines; good durability; low viscosity; low resistance to high temperatures and impact; requires no pressure during cure; presents negligible shrinkage during curing	Very useful for bonding metals to other substrates. Bonding of metal, ceramic and glass. Quick mounting of lightweight structures
Polyaromatic	Excellent resistance to extreme temperatures. Difficult to process	Bonding of metal, ceramic and composites in aeronautical and aerospace applications
PUR	High dry and wet strength; good adhesion to concrete, wood, metals, glass, ceramic and plastics; resistant to water and humidity; formulations with diverse cure times; excellent resistance to impact; excellent flexibility at low temperatures; moderate resistance to prolonged and repeated exposure to wet and drying periods. Gap-filling properties	Bonding of floors and wall components. Bonding PW to metal and plastic sheets. Used in some laminated components in boats and planes. Repair of structural and decorative elements. Repair of laminated timber beams
PVAC-R	High dry strength; poor resistance to water, high humidity and high temperature; moderate resistance to oils, fat and acids. Gap-filling properties	PW (hardwoods), interior and exterior doors. Decorative wood structures. Some formulations are used to bond hardened concrete to fresh or hardened concrete
Polyesters (unsaturated)	High shrinkage during cure; moderate resistance to chemicals, moisture, high temperature and ageing; various formulations with wide levels of strength; formulations containing isocyanates adhere well to plastics. Gap-filling properties	Bonding of various materials (concrete, metal, plastic, glass, etc.). The bonding to concrete usually requires a primer. Should not be used when the substrate is damp or wet. Some formulations are used for bonding steel to concrete (e.g. anchors, reinforcement elements, protection elements) in the repair of cracks in concrete or masonry and in the strengthening of masonry structures

Note: *PW* plywood

16.3 Adhesion

16.3.1 Definition of the Phenomenon

Bonding technology has been studied since the last century and has played a key role in increasing the use of bonded connections, replacing or complementing the mechanical connections, in several industries and more recently in the construction sector.

Obtaining a quality bond depends on the degree of knowledge and control of all factors that constitute and influence the bonding process. The existence of a large number of construction materials to bond, as well as the constant development of new types or formulations of structural adhesives and building materials, has contributed to the advancement of knowledge on the properties and modes of action of adhesives.

Bonding technology can be divided into two parts: the formation of the bonded joint and the performance of the bonded joint. The formation of bonded joint is related to the properties of adhesives as liquids, which must possess properties that enable them to achieve the proximity necessary for adhesion to occur and allow them to be properly converted into solids. The performance of the bonded joint is related to the properties of the adhesives as solids and in particular their response to applied stresses and exposure to degradation agents (temperature, humidity or water, solar radiation, chemicals, etc.). As the performance of the bonded joint is also affected by how it is produced, the two parts are co-dependent. Moreover, because of the tensions that are created in the bonded joint and/or transferred through it, typically in a non-uniform way, it is possible that the bonded joint has a satisfactory performance but the final bonded connection has not; therefore, it is necessary to consider a third part, the performance of the bonded connection [41].

Considering the bonding process as a sequence of events and identifying the factors that influence and constrain each of them, these factors can be grouped into six categories. The sum of these categories to the adhesion forces produced by adhesives allows representing the performance of a bonded connection by Eq. (16.1) [41].

$$\begin{aligned} &\begin{array}{l}\textbf{Performance}\\ \textbf{of a bonded}\\ \textbf{connection}\end{array} = \begin{array}{l}\text{Adhesion}\\ \text{forces}\end{array} \pm \underset{\text{(Category 1)}}{\begin{array}{l}\text{Factors related}\\ \text{with the}\\ \text{adhesive composition}\end{array}} \pm \underset{\text{(Category 2)}}{\begin{array}{l}\text{Factors}\\ \text{related to}\\ \text{the substrate}\\ \text{mechanical}\\ \text{properties}\end{array}} \\ &\pm \underset{\text{(Category 3)}}{\begin{array}{l}\text{Factors}\\ \text{related with}\\ \text{the substrate}\\ \text{preparation}\end{array}} \pm \underset{\text{(Category 4)}}{\begin{array}{l}\text{Factors}\\ \text{related with}\\ \text{the adhesive}\\ \text{application}\end{array}} \pm \underset{\text{(Category 5)}}{\begin{array}{l}\text{Factors}\\ \text{related with}\\ \text{the bonded}\\ \text{joint}\\ \text{geometry}\end{array}} \pm \underset{\text{(Category 6)}}{\begin{array}{l}\text{Factors}\\ \text{related with}\\ \text{service}\\ \text{conditions}\end{array}} \end{aligned} \tag{16.1}$$

The first four categories of the performance equation of bonded connections affect the formation of the bonded joint. The fifth category affects the formation and the performance of the bonded joint. The sixth category affects only the performance of the bonded joint [41].

The first category is related to the choice of a particular adhesive for the application concerned, since the adhesive composition will affect its properties. Thus, this category includes factors such as viscosity, cure type, strength, degree of shrinkage occurred during curing, surface tension, filler content and components. The second category is related to the properties of the substrate that will give the desired strength, performance and durability to the bonded connection. For example, a bonded timber connection includes factors as the wood species, strength, density, dimensional stability, permeability and durability. The third category is related to the quality of the surface to be bonded, which includes all factors that derive from the substrate preparation, for example, the surface cohesion state, water content and presence of contaminants. The fourth category relates to the preparation and application of the adhesive, including factors such as ratio between resin and hardener, method of mixing the adhesive components, temperature and relative humidity at the time of bonding and during curing, application method and applied pressure. The fifth category is related to the geometry of the bonded joint, including the factors that will control the quantity and type of stresses applied to the bonded joint, for example, the substrate dimension, the structure (homogeneous, heterogeneous, laminated, etc.), the shape (flat, curved, irregular, etc.) and variability. The sixth and final category encompasses all the factors that act on the final bonded joint during service life, for example, type, magnitude and duration of mechanical actions (e.g. static loads, dynamic loads, mixed loads, accidental impacts, natural disasters) and exposure to degradation agents (temperature, humidity, chemicals, radiation, etc.) [41].

Adhesion, as mentioned before, is defined as the phenomenon in which two surfaces are held together by chemical, physical or physico-chemical forces resulting from the presence of an adhesive. Therefore, in order to obtain a good quality bonded joint, it is essential that there is good contact between the adhesive and the substrate and that the surface of the latter is free from contaminants, has a cohesive structure and is well connected to its interior.

16.3.2 Explanatory Theories

Adhesion is a complex phenomenon and, although extensively studied, is not yet possible to define it completely. Although there are several theories that attempt to explain this phenomenon, there is none able to explain it universally. For this reason, the theory or theories that best explain the phenomenon of adhesion will vary according to the type of substrate and adhesive involved in the particular application.

Among the various theories of adhesion, the most consensual are: (a) mechanical (or mechanical interlocking) theory; (b) adsorption (or thermodynamic) theory; (c) chemical bonding theory; (d) diffusion theory; (e) electrostatic (or electronic) theory; and (f) theory of weak boundary layer [2, 3, 10–12, 21, 22, 42–44]. Table 16.11 describes the characteristics of the interactions involved in the various adhesion theories.

Table 16.11 Description of the types and characteristics of the interactions involved in adhesion [3, 21, 42, 43, 45]

Theory of adhesion	Interaction	Energy (kJ/mol)	Distance	Scale
Mechanical theory	Mechanical	–	10 nm–2 mm	Microscopic
Diffusion theory	Mechanical	–	10 nm–2 mm[a]	Molecular
Electrostatic theory	Charge	600–1,000	100–1,000 nm	Macroscopic
Physical adsorption theory				
Van der Waals interactions[c]	Charge			Atomic/ molecular
Dipole-dipole forces (Keesom)		4–20	0.5 nm	
Dipole-induced dipole forces (Debye)		<2	1.0 nm	
Dispersion forces (London)		0.08–40	1.0 nm	
Hydrogen bonds (excluding fluorines)[c]		<50	0.3–1.0 nm	
Lewis acid–base interactions[c]		<80	0.6–2.0 nm	
Chemical bonding theory				
Ionic bonds[b]	Charge	600–1,100	0.2–0.4 nm	Atomic
Covalent bonds[b]		60–700	0.1–0.2 nm	
Brønsted acid–base interactions[b]		<1,000	0.1–0.4 nm	
Weak boundary layer theory	Mechanical	–	1–100 nm	Molecular

Note:
[a] Depends on the thickness of the interphase
[b] Primary bonds involving first-order forces (intramolecular)
[c] Secondary bonds involving second-order forces (intra- or intermolecular)

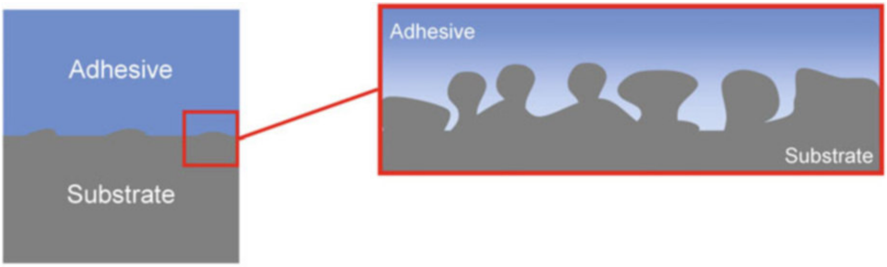

Fig. 16.6 Schematic explanation of the theory of adhesion by mechanical mechanisms (adapted from [54])

The *mechanical theory* proposed by MacBain and Hopkins in 1925 [46] assigns the adhesion to the fact that the adhesive penetrates into the pores, cavities, cracks and other irregularities of the substrate surface and then solidifies, being the adhesive mechanically "anchored" or "locked" in the substrate (Fig. 16.6). In order to produce a good adhesion, it is necessary that the adhesive adequately wets the substrate (factor that depends on its surface tension) and penetrates into the irregularities of the substrate (factor that depends on its rheological properties) prior to solidify. The fact that the vast majority of adhesives produces a superior adhesion when applied to rough or porous substrates, compared with that obtained when applied to substrates of smooth surfaces, contributes to the acceptance of this theory. However, as it is also possible to obtain a good adhesion on smooth surfaces, this theory is not universal. Thus, this mechanism can contribute to the final strength of the bonded joint in more or less extent depending on the specific situation. The fact that adhesion improves with surface treatments that result in increased roughness of the substrate surface may be due not only to mechanical "interlocking" but also to the formation of a surface clean of impurities, to the removal of a superficial layer that is cohesively weak and/or poorly attached to the underlying substrate and to the formation of a surface with a larger contact area or by the formation of a chemically different surface that is more receptive to the adhesive. In this way, if the adhesion results from the formation of intermolecular forces between the adhesive and the substrate then, by increasing the contact area between them, the effective total area over which bonds can be established is being increased; thus, the adhesion improvement results from the higher number of forces which have been developed and not from the increase of the mechanical interlocking. Nevertheless, the mechanical anchorage provides additional benefits to the bonded joint, for example, the roughness is a barrier to crack propagation, and the interphase created by adhesive in the interstitial spaces of the substrate allows the bonded joint to more effectively dissipate the stresses exerted on it through viscoelastic or elastic deformation of the adhesive. This mechanical interlocking gives to the bond line a high resistance to shear stress, but a poor resistance to tensions normal to the surface. In the case of porous substrates, like wood and concrete, it is thought that mechanical mechanisms will contribute more significantly to the ultimate strength of the bonded joint than the physico-chemical mechanisms (adhesion forces between adhesive and substrate) [2, 14, 22, 43, 47–53].

The theory of physical adsorption (or thermodynamic), attributed to Sharpe and Schonhorn [55], assumes the development of van der Waals bonds (dipole-dipole forces, dipole-induced dipole forces and dispersion forces) and hydrogen bonds between the adhesive and substrate. In this way, the adhesion is produced by bonds of second order (Fig. 16.7). For these forces not to be negligible, it is necessary that the molecules of both have a distance smaller than 1.0–2.0 nm ($1.0–2.0 \times 10^{-9}$ m). For this to happen, it is necessary that the adhesive adequately wets the substrate surface, displacing all or almost all the air present in the interface, so as to form a continuous surface and avoid creating stress concentration areas (which may occur in places where some air is retained). For the adhesive to wet the substrate, it is necessary that its surface tension is less than that of the substrate. For example, most organic adhesives readily wet the metal surfaces, but the same doesn't happen with organic substrates since many of them have a very low surface energy (polyethylene, polypropylene, wood, poly(tetrafluoroethylene), etc.). Such bonds are of low intensity (Table 16.11), but, due to high number of bonds that usually are formed,

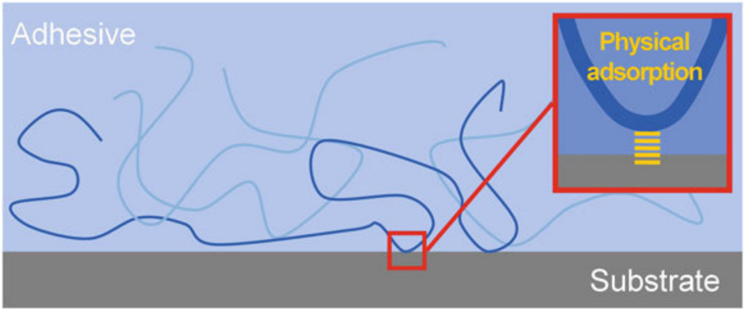

Fig. 16.7 Schematic explanation of the theory of adhesion by physical adsorption (adapted from [61])

they may be sufficient to produce a bonded joint with a good strength [2, 14, 22, 43, 49, 56–60].

The *chemical bonding theory* is very similar to the previous one, differing only in the type of interactions that are developed between the adhesive and the substrate. In this case, it is assumed that the adhesion is produced by forming chemical bonds, which can be covalent, ionic or result of the Brønsted acid–base interactions between the adhesive and the substrate. Thus, the adhesion is produced firstly by adsorption of the adhesive molecules at the surface of the substrate and secondly by the formation of chemical bonds between the molecules of both (Fig. 16.8). As in the previous case, it is also necessary that the adhesive adequately wets the substrate surface so that the molecules of both stand closer than 0.4 nm (0.4×10^{-9} m). The existence of Brønsted acid–base interactions depend on the type of adhesive and type of substrate. The existence of covalent bonds was only occasionally demonstrated in some specific applications, for example, between the amine groups of the hardener of an epoxy adhesive and the surface of PE and PP treated with fluorine [3] and between polysulphide and brass [2]. The use of adhesion promoters in bonded connections has been a way of trying to take advantage of the chemical bonds [62, 63]. The ionic bond may occur, for example, among an ammonium group and a carboxylate group. The Brønsted acid–base interactions between cations and anions may occur, for example, in wood, since it contains carboxylic acids that may form salts with adhesives that contain basic groups, such as amine groups present in MF adhesives, in protein adhesives and EP cured with amines. The primary bonds are stronger than secondary bonds (Table 16.11) and so they produce a bonded joint with higher strength and durability [2, 12, 14, 22, 43, 62–66].

The *electrostatic* (or electronic) theory proposed in 1948 by Deryaguin [68] assumes that if the adhesive and the substrate have different electronic structures, when brought into contact, an exchange of electrons between them may occur, in an attempt to balance the Fermi levels, forming a double electrical layer at the interface (Fig. 16.9). After this layer is formed, and so that it is possible to separate the adhesive and the substrate, it will be necessary to overcome the electrostatic

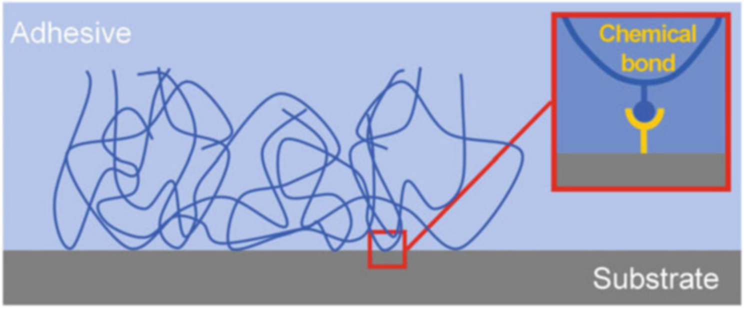

Fig. 16.8 Schematic explanation of the theory of adhesion by chemical bonds (adapted from [67])

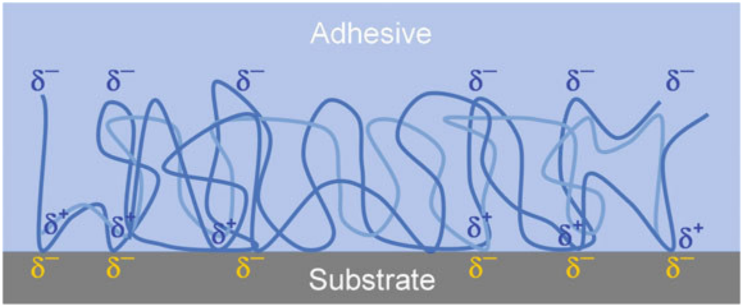

Fig. 16.9 Schematic explanation of the theory of adhesion by electrostatic forces (adapted from [73])

attraction present in the double electrical layer. The separation will cause a potential difference between the adhesive and the substrate, which will increase until an electric discharge occurs at the time the bond is broken. Thus, according to this theory, the adhesion is produced by electrostatic forces generated because the adhesive and the substrate remain with opposite electric charges. Today, this theory is only taken into account to explain the adhesion produced between pressure-sensitive adhesives and metal substrates and needs further studies to confirm and clarify the phenomena involved [2, 22, 50, 69–72].

The *diffusion theory* proposed by Voyutskii in 1962 [74], but which acceptance is also due to the work of Vasenin [75], assumes that when the adhesive and the substrate are brought into contact, there is a migration, through the interface, of molecular chains or segments of molecular chains of the adhesive to the substrate and vice versa, creating an interphase where the adhesive and the substrate are mechanically linked (Fig. 16.10). Thus, the adhesion produced from a material to itself ("autohesion" or "auto-adhesion") or to other material ("heterohesion" or "hetero-adhesion") is due to mutual diffusion (self-diffusion or interdiffusion, respectively) of molecular chains or molecular chain segments. This theory was

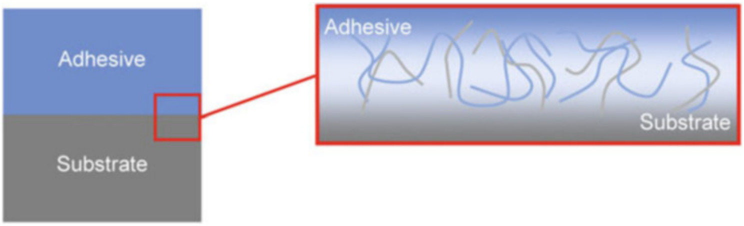

Fig. 16.10 Schematic explanation of the theory of adhesion by diffusion phenomena (adapted of [80])

first proposed to explain the observed adhesion between elastomers with similar chemical compositions and at temperatures higher than the glass transition temperature. Today, this theory is considered valid for polymeric materials, but only to explain the "autohesion", the welding of identical thermoplastics by heat or solvent and the self-healing of polymers. Moreover, this theory requires that the polymers of the adhesive and the substrate have mobility, be compatible and miscible. This theory does not apply in situations in which the adhesive and the substrate are not soluble, when the molecular mobility is restricted by its crystalline or cross-linked structure, or when the materials are at a temperature far below its glass transition temperature [2, 22, 76–79].

The *weak boundary layer theory*, although not exactly an adhesion theory, is generally regarded as such, was proposed in 1961 by Bikerman [81] and assumes that the rupture of a bonded joint is always due to the presence at the interface of a layer that is mechanically weaker than the adhesive and the substrate. This theory suggests that the breakage of a bonded joint always happens cohesively in the adhesive or in the substrate, i.e. close to the interface but not on the interface itself, although it may appear so, due to the very small thickness of that layer. In this sense, the cohesion of this weak boundary layer determines the magnitude of adhesion produced. This theory is based upon statistical considerations that suggested that there was a low probability of the rupture to extend through the interface, but high probability of the rupture to occur in the weaker material and close to the interface. The experimental evidence does not support this theory, since it shows that in some situations it is possible that a rupture occurs at the interface. Furthermore, the fact that a cohesive rupture occurs in the adhesive or in the substrate near the interface does not necessarily mean that there is a weak boundary layer. Although this theory does not help to understand how and why adhesion is produced, it is useful to understand why a bonded joint may not behave appropriately. If any, these weak boundary layers may originate in the substrate or in the adhesive, and may be formed before bonding, during application of the adhesive, during solidification or in service [2, 14, 22, 43, 82–88].

Given the above, it appears that adhesion is indeed a complex phenomenon that cannot be interpreted using only a theory or model. Given the multiplicity of processes, materials and factors involved in adhesion, the search for a universal theory that can explain all the experimental facts is an unprofitable task because all theories have a domain of validity, depending on the nature of the adhesive and the substrate and the conditions of formation of the bonded joint. Although, in reality there are several mechanisms simultaneously involved, nowadays, it is assumed that the adsorption (or thermodynamic) theory is the one that has a greater applicability because it considers that it is necessary for the adhesive to establish an intimate contact with the substrate so that the physical forces of attraction may develop at the interface. Moreover, this is a prerequisite for the subsequent occurrence of mechanical mechanisms, diffusion mechanisms and, eventually, primary bonds that will strengthen the bonded joint.

16.4 Bonded Connection

The attainment of a bonded connection is normally considered a process that involves the following stages: (1) selection of the bonding system; (2) design of the bonded connection; (3) preparation of the surfaces to be bonded; (4) fabrication of the bonded connection; (5) process control; and (6) monitoring the behaviour of the bonded connection in service. All these steps are critical to obtain a quality-bonded connection, so none should be neglected. Furthermore, it is very important that throughout the process of obtaining a bonded connection there is communication between the various parties involved, namely the designer, the bonding system manufacturer/supplier, the civil engineer, the architect, the contractor, etc. [3, 10–13, 21, 89–97].

16.4.1 Selection of the Bonding System

The first step in obtaining the bonded connection consists in choosing the type of adhesive product more suitable for the application concerned.

Selecting an adhesive is a difficult procedure due to the large number of factors that must be considered, especially since there is no universal adhesive applicable in all situations. The various families of adhesives tend to overlap concerning the characteristics. In this way, adhesives from different families may present similar properties or the inverse, i.e. a family may include adhesives with very different properties.

In general, given the wide variety of adhesives that exist, it is necessary to reach a compromise when choosing a particular adhesive for a specific application, given that, among the various properties and desired features, some are more relevant than others. Therefore, it is essential to define which are the most important characteristics for the application concerned.

When selecting an adhesive, it must be taken into account that this choice should allow not only to satisfy the requirements, as to the characteristics that the adhesive must present, but also allow to optimise the entire process of obtaining a bonded connection. Therefore, the choice must also take into account the other stages of the process. It is important to take into account, for example, the method of application and curing conditions of the adhesive, the preparation method of the surfaces to be bonded, the joint geometry, the acting stresses, the environmental conditions, the quality control and the monitoring of the bonded connection during service. Although it appears impossible to satisfy all these requirements, given the existence of numerous types of adhesives, each with several different formulations, it is generally possible to find a good solution.

There are several methodologies for choosing an adhesive for a specific application. One is to first consider the function or application field in question (structural, semi-structural, non-structural) and to then consider the durability that it must present in the service conditions to which the bonded connection will be exposed (e.g. service class in the case of timber structures). These two steps can be performed by consulting reference tables like those presented in this chapter in Sect. 16.2.1.3 (Table 16.4) and Sect. 16.2.1.6 (Table 16.6), information available in the literature (see Sect. 16.8.1), adhesive selection tables provided by manufacturers [98] and also by using specific software or online applications (e.g. *The Adhesives Design Toolkit* [99], *Adhesion Selector* [100]).

By using the above procedure, it is possible to reduce the vast number of commercial adhesive products available to just a few. To further reduce the number of possible adhesives for the application in question, other factors must be considered such as: (a) type of substrate; (b) type, magnitude and duration of the applied loads; (c) thickness of the bond line; (d) environmental conditions in which it will be applied and solidify; (e) special requisites of the application in question (e.g. thixotropy, gap-filling properties, slow/fast cure, cure at low temperatures); (f) special restrictions of health and safety.

Once the adhesive systems are selected according to these general factors and the bonded connection project is completed, it is then possible to choose the final product, specific for the application concerned. This last step of the procedure of selecting the adhesive product must be made with the supplier/producer of the product, since that only him can specify the formulation, the method of preparation of the substrate, the physical form of the product and the conditions of application and curing more adjusted to the product and the application in question, as well as pointing any other additional requirements that might exist.

Depending on the application in question, it may still be necessary to test the bonding system and the method of application before it is applied to the structure. This is done, for example, in less common situations for which previous experience does not exist in order to guarantee that the bonded connection will present the performance and durability foreseen in the project.

Section 16.8.1, of this chapter, presents some references where the reader can obtain information on the characteristics of several bonding systems, as well as normative documents where it is possible to find adhesive specifications for some applications.

Table 16.12 Indicative design working life categories according to EN 1990 (adapted from [101])

Design working life		
Category	Duration (years)	Examples
1	10	Temporary structures[a]
2	10 to 25	Replaceable structural parts
3	15 to 30	Agricultural and similar structures
4	50	Buildings and other common structures
5	100	Monumental buildings, bridges and other special structures

Note: [a]Structures or parts of structures that can be dismantled to be reused do not belong in this category

16.4.2 Design of the Bonded Connection

The knowledge of the general properties and characteristics of the adhesive allows to design the bonded connection in an adequate way, guaranteeing that the acting tensions are inferior to the resistant tensions of the bonded joint, and that the effect of the load duration and the environmental conditions in the bonded connection are correctly taken into account when the connection is detailed. As it was already noted, the project must guarantee that the proposed geometry for the bonded connection maximises the bonding area and introduces the tensions in the direction of the maximum strength of the bonded joint (shear or compression). It must also prevent the introduction of peel or cleavage tensions in the bonded joint, guarantee a continuous and uniform bond line and assure a uniform distribution of the applied tensions, in order to prevent the concentration of tensions in the bonded joint that can lead to its premature failure. Furthermore, the project must consider the weak resistance that adhesive products offer against extreme situations (e.g. fire) and allow and facilitate the fast and efficient fabrication of the bonded joint (e.g. leaving enough space to allow the preparation of the surface, the application of the products and their maintenance in place during application and cure). Ideally, the project should consider the possibility of a final quality control (involving or not a test of the bonding strength), periodic inspections to evaluate the condition of the bonded connection in service and, possibly, future interventions of maintenance/repair of the bonded connection.

Generally, in the case of a new structure, the working life of the bonded connection should be equal to the working life of the element or structure on which it is applied. However, considering the various categories for the working life of the element or structure defined in the European standard EN 1990 [101] (Table 16.12), it is observed that in some applications the project should specify an adhesive that produces a highly durable bonded connection. Due to the relatively recent use of these products in the construction sector, despite similar products have been used for a long time in other industries (e.g. aeronautics), and to the lack of standards that define reliable and realistic methods of evaluating the durability of bonded connections, it is sometimes difficult to guarantee the desired durability in certain applications, thus compromising the use of these systems. Nevertheless, this limitation can be overcome if the bonded connections are used in temporary structures, in elements that can be replaced during the life of the structure, or in structures where it is possible to inspect and repair the connections during their working life.

The design of structural elements shall comply with the legal or regulatory framework in force in the specific country. The specific framework varies depending on the construction material involved, and it can be found in the chapters in this book in which they are addressed individually (“**Concrete”, “Steel”, “Wood”, “Fibre-Reinforced Polymer Composites”**). In this chapter it is important to note that, currently, there are no Portuguese or international standards specifically dedicated to the design of bonded connections and that this information is scattered in the literature and, as such, lacks uniformity and favours the existence of ambiguities, due the multiplicity of products and fields of application covered. In spite of this, Sect. 16.8.2 of this chapter indicates where it is possible to find information on the design of structural bonded connections. That section also presents the most important standards concerning the use of adhesives in construction.

16.4.3 Preparation of Surfaces to Be Bonded

The adequate preparation of the surface to be bonded is one of the most important stages of the bonding process, fundamental for the bonded connection produced to behave efficiently. As it was previously noted, in the description of adhesion theories, the adequate treatment of the surfaces of the materials to bond is essential to obtain a bonded joint with a good initial strength and a good long-term performance, particularly, in situations in which the bonded joint will be exposed to harsh service conditions.

The preparation of the surface to be bonded involves the execution of tasks that depend on the type of substrate and the specific application. The most common are the removal of contaminants (e.g. fats, oils, rust), the removal of any superficial layers with weak cohesion and/or adhesion to the underlying base material (e.g. superficial layer of degraded substrate, pre-existing coatings) and the removal of any chemical products resulting from the preparation of the material to be bonded (e.g. solvents), in the drying of the surface to be bonded, in the determination of the surface condition, in the increase of the surface roughness, in the production of a continuous adhesive line with a uniform thickness and in the application of primers or other surface treatments.

Given the multiplicity of materials, combinations of materials and connection geometries used in the most diverse applications, the available recommendations in literature are of general nature. Therefore, it is always necessary to decide with the producers and/or suppliers of the adhesive products which is the best methodology for the application in question. The factors that must be considered when selecting the surface preparation method are initial strength, durability, initial condition of substrate, type and nature of its surface and factors of practical order (e.g. available space, reproducibility) and of economic order (e.g. duration of the operation, cost of the materials and the equipment involved).

In some cases, given the specificity of the application, it may be necessary to make tests to confirm the effectiveness of the preparation methods.

In view of the above, it is easy to conclude that the necessity of surface preparation also constitutes a factor that must be weighed at the moment of selection of the bonding system, since that a lesser sensitivity presented by a determined product compared to other products regarding the condition of the substrate can be considered as a preferential factor in its choice.

Section 16.8.3 of this chapter presents references where the reader can obtain more information regarding the main methods of surface preparation of substrates.

16.4.4 Fabrication of the Connection

The production of a bonded connection involves the storage, preparation, application and the curing of the bonding system. It is convenient that all these steps are carried out by operators, adequately trained, under the watchful supervision of a qualified person and in accordance with the manufacturer indications, because only then is possible to guarantee that the production of the bonded joint will happen in the best possible way.

Normally, all adhesive products present a time interval during which they preserve their initial characteristics intact, as long as they are subjected to certain environmental conditions—storage life. In the case of not complying with the environmental conditions specified in the product sheet during this period or if this period is exceeded, the adhesive products can suffer irreversible physical and/or chemical alterations that will strongly compromise their performance and durability; therefore, their use is not recommended. Storage periods vary according to the specific product, but in general, they can go from some months until 1 or 2 years.

Apart from being necessary to fulfil the time and storage conditions, it is also necessary to confirm if the product packing is in perfect conditions before, during and after the storage, for this is the only possible way to guarantee that the products are in conditions of being used.

The place of application of the bonding system must be kept clean during and after the preparation of the surfaces to be bonded and, when using chemical products, necessary measures must be taken so that there are no vestiges in the environment, especially if volatile products are used. It is also important that the application site is sufficiently ventilated so that no harmful environments to human health are created, since some bonding systems have toxic or volatile components that will be released into the atmosphere when prepared and applied.

The most frequent errors found in this stage are non-compliance with the specified ratio of the adhesive product components, resulting from the disrespect of the recommended values or from an erroneous weighing of the individual components; non-compliance with the maximum volumes of the products that can be used, which can lead to the release of excessive heat during curing and, therefore, produce an adhesive with properties inferior to those expected; the use of a mixing method of the components different of the one specified, resulting in a heterogeneous product that will not cure properly or in a product that will present a performance inferior to the expected; non-compliance with the temperature (of air, of the substrate or of the adhesive products), with the relative humidity of air and/or water content of the substrate, specified in the technical data sheet of the product; non-compliance with the open assembly time and the adhesive pot life; the use of insufficient volume of adhesive per bonded joint; non-compliance with the specified thickness of the adhesive line; non-uniform adhesive line; application of insufficient pressure to join the materials to bond; and removal of the support and fixing systems before the adhesive cure is complete.

In some situations, it may be necessary to control the temperature of the place of application of the bonding systems and/or to make a previous conditioning of these so that they reach the required temperature and are able to be correctly prepared and applied. The conditioning of the environment must be kept during the preparation, application and curing of the bonding systems, so that they don't exceed neither the minimum nor the maximum temperature indicated by the manufacturer. This is necessary to guarantee that an adhesive with the properties below the expected is not produced because it does not reach the required degree of curing or because it degrades itself.

A valid recommendation for all situations is that once the surfaces to be bonded are prepared, the application of the bonding systems should be done as soon as possible, in order to prevent new contamination.

Finally, the work must be executed in accordance with the current legislation concerning health safety, and in accordance with the health and safety plan defined in the project. All the bonding systems possess a safety data sheet, containing information on its composition, associated risks, handling procedures, need of special clothing and protection equipment and procedures to follow in case of accident, among other security recommendations.

16.4.5 Process Control

The application requirements of the products that compose these systems, as well as the specificity of the interventions, imply the adoption of a set of measures capable of guaranteeing the quality of the work executed and the effectiveness of the interventions. In addition to the factors already referred to (e.g. proper selection of materials, careful design according the objectives and specificity of work, use of skilled labour adequately alerted to the implications arising from inappropriate procedures or non-compliance with security rules), it is also essential to elaborate and implement a quality plan.

The quality plan should be complete, but as simple and objective as possible, and able to guarantee the systematic verification of all the work variables susceptible of compromising the effectiveness of the system.

The quality plan must comprise, among others: (a) a detailed record with information concerning materials, equipment, methods and the intervention made to prepare the surfaces to bond; (b) a detailed record with information concerning the materials, equipment, methods and intervention made to fabricate the bonded connection; (c) a planning for the execution of quick tests to detect the existence of eventual deficiencies that may occur during the preparation of the surfaces to bond and during the production of the bonded connection [102].

A detailed record is important because it allows detecting in real time possible errors or omissions, sometimes with serious implications, and identifying the origin of eventual anomalies that appear a posteriori.

The quick tests for quality control can be made either on the bonding systems or on the bonded joint and, according to the application, they can be destructive or not. Given the great variety of tests that are possible to carry out, the choice must have into account that these must allow to determine in a simple, fast and reproducible way parameters that are later directly related with the intended properties to control.

Finally, it is essential that during the on-site production of the bonded connection, an inspection programme is implemented and adjusted to confirm if the project and the procedures recommended by the bonding products manufacturer have been meticulously followed. This programme must include sampling and tests/measurements on site and/or at laboratory and a set of procedures in case of non-compliance with the project and with the manufacturer’s recommendations.

Section 16.8.4 of this chapter presents references where the reader can find further information regarding the main testing methods used in process control.

16.5 Performance and Durability

Despite being relatively easy to obtain bonded connections with a good initial resistance, in some situations it is more difficult to obtain bonded connections with a good durability. In the case of structural bonded connections, durability has an even higher importance, since the connection participates in the integrity of the structure and therefore has to be capable of supporting high loads during long periods, sometimes, in very demanding service conditions.

The main degradation factors affecting the durability of bonded connections can be grouped into three categories, according to their origin, namely environment, materials and mechanical actions.

Environmental degradation factors include: temperature (e.g. extreme temperatures, thermal cycles, fire), moisture and/or the presence of water (e.g. immersion in water, wetting-drying cycles, relative humidity, humidity cycles), chemical products from the environment (e.g. contaminated waters, pollution) or from the substrate (e.g. alkaline environment in concrete, extractives in wood, corrosion in metals), radiation (e.g. solar), maritime environment and biological agents (that may affect the adhesive and/or the substrate) [2, 3, 10, 12, 13, 21, 22, 89, 103].

Degradation factors originated in the materials involved in the bonded connection include the substrate, the adhesive and the interphase between both.

The last category refers to the degradation factors originated by mechanical actions, including static loads (e.g. creep), dynamic loads (e.g. fatigue), combined loads, impacts, earthquakes and other environmental disasters. In this category it should be noted that the tensions exerted on the bonded connection may have an internal origin (i.e. in the adhesive or in the substrate) or external origin (i.e. stresses originating within the structure or as a result of loads being applied to the structure) [2, 3, 10, 12, 13, 21, 22, 89, 103].

The study of performance and durability of structural bonded connections is extremely important because, as already mentioned, the bonded connection has to maintain its physical and chemical integrity over the lifetime of the structure in which it is applied. As seen previously, the durability of a bonded connection is determined not only by the nature of its constituents and the quality of their preparation and application but also by the action of environmental and mechanical degradation factors acting on the bonded joint throughout its working life. Thus, to understand how the bonded joint can successfully carry out its role during the period for which it was designed, it is necessary to know the degradation mechanisms of the bonded connections constituent materials in the environment in question. For this purpose, chemical, physical and mechanical characterisation and durability tests of adhesives and bonded connections are used. Therefore, in order to be able to determine correctly the performance and durability of a bonded connection, it is imperative to assess bonded joints prepared with adhesives and specific substrates, subjected to loading speeds and modes and environmental conditions that replicate, as much as possible, the conditions that the bonded connection will face while on service [2, 3, 10, 12, 13, 21, 22, 89, 103].

Currently, there are several standardised tests for the characterisation of bonded connections. However, since the results obtained through these tests cannot be directly transposed in strength values for a particular bonded connection designed for a specific application, the best thing that can be done is to test the real bonded connection in laboratory under conditions that approach as much as possible those found in service. Therefore, it is important to understand what are the usefulness and limitations of the various tests specified in the standards before choosing a particular test plan for the specific application(s) concerned. In some situations, it may be necessary to develop a new test method to comply with the specific requirements of the project in question.

Given the general nature of the topics covered in this chapter, there will be no analysis of the influence of the degradation factors described above in the materials that may be involved in bonded connections. Such approach will be made in each of the chapters specific to each construction material (**“Concrete”, “Steel”, “Wood”, “Fibre-Reinforced Polymer Composites”**). Section 16.8.5 provides several references where the reader may obtain detailed information concerning the performance and durability of adhesives and bonded connections.

16.6 Applications

Tables 16.13, 16.14, and 16.15 summarise the main applications of adhesive products in civil engineering. Section 16.8.6 presents several references where more information can be found on this subject.

Table 16.13 Main applications of adhesive products in maintenance interventions [13, 39, 90, 104–109]

Field of application	Substrate	Application
Maintenance (conservation/ repair)	Concrete	Repair of stabilised fissures, cracks or cavities of significant dimensions to re-establish the monolithic nature and the tightness of the element (e.g. cracks caused by shrinkage, movements of foundations, bad execution of concrete joints)
		Repair of active fissures or cracks creating an expansion joint (e.g. cracks deriving from thermal actions)
		Repair of deteriorated structural elements through the reconstruction of part of the structural element (e.g. repair of structures in which it is required a very rapid cure; repair of small thicknesses, <30 mm, or angular zones of structures)
	Timber	Repairing of cracks and delaminations (e.g. injecting adhesive in cracks, crack sealing with bonded timber wedge/fillet)
		Repair of deteriorated structural elements through reconstruction or localised replacement of part of the structural element (e.g. repair of a beam end by means of bonded prostheses)
		Repair of deteriorated connections between elements through the reconstruction or localised replacement of part of the structural element (e.g. repair of connections in king post trusses)
	Other	Reconstitution of rocks of different natures
		Protective coatings (e.g. impregnations for regenerating porous or friable surfaces—stone, bricks, deteriorated timber, etc.; reinforced coatings, to provide tightness to fissured zones)

Table 16.14 Main applications of adhesive products in rehabilitation interventions [13, 39, 90, 104–109]

Field of application	Substrate	Application
Rehabilitation (reconversion/ requalification)	Concrete	Reinforcement of structural elements by external bonding of metallic materials (e.g. flexural reinforcement of beams or slabs through the bonding of steel plates)
		Strengthening of structural elements by internal or external bonding of fibre-reinforced polymer composites materials (e.g. seismic retrofitting of structures; flexural or shear strengthening of beams by bonding FRP strips, fabrics or sheets; flexural reinforcement of slabs by bonding FRP strips; strengthening of columns through the bonding of FRP strips, fabrics or sheets)
		Reinforcement of structural elements by external bonding of prestressed fibre-reinforced polymer composite materials (e.g. flexural reinforcement of beams by bonding prestressed FRP strips)
	Timber	Strengthening of structural elements by internal or external bonding of metallic materials or fibre-reinforced polymer composite materials (e.g. tension and/or compression zone upgrading of floor beams or truss components)
		Strengthening of connections between structural elements by internal or external bonding of metallic materials or fibre-reinforced polymer composite materials (e.g. strengthening of connections between truss components, strengthening of traditional timber mortise and tenon joints by bonded-in rods)
		Perpendicular to wood grain reinforcement of the structural element by internal or external bonding of metallic or fibre-reinforced polymer composite materials (e.g. reinforcement of timber and glulam beams, to avoid splitting along the grain, with FRP rods, fabrics or sheets)
	Masonry	Increase of the element's strength through confinement (e.g. compression strengthening of pilasters or spandrels through confinement using external bonding of FRP sheets or fabrics)
		Increase of the element's strength by adding a new material (e.g. flexural or tensile reinforcement of walls and vaults through the surface bonding of FRP sheets or fabrics)
		Local increase of element's strength through the reconstruction of its section using another material (e.g. repairing cracks, fractures, local deformations or cave-ins on walls or vaults through the bonding of FRP fabric in local lesions)

Table 16.15 Main applications of adhesive products in new constructions [13, 39, 90, 104–109]

Field of application	Application
Construction (new structures)	Bonding of prefabricated heavy concrete elements (e.g. segmental bridge construction)
	Bonding of fresh concrete to hardened concrete
	Bonding of hardened concrete to hardened concrete
	Bonding of anchorage to concrete, masonry or rock
	Bonding of prestressed anchorage to concrete, masonry or rock
	Used as shear connectors in composite structures (e.g. used in timber-concrete or steel-concrete structures as an alternative to metal connectors)
	Used in the fixation of metal or composite connectors between structural elements (e.g. connection between beams of timber or materials obtained from glued solid timber, connection between structural composite elements)
	Protective coatings
	Injection in concrete areas which have empty spaces (e.g. filling of cavities present in concrete due to poor vibration, filling of cavities present in concrete in heavily reinforced areas)
	Wood-based materials. Wood-based panels (e.g. plywood, oriented strand board) are used in applications that require large areas and small thicknesses. Examples of structural applications include formwork, vertical web in I beams, exterior cladding, panels for partitions, etc. Materials considered as reconstituted solid wood (e.g. solid wood panels, SWP; glued-laminated timber, glulam; laminated veneer lumber, LVL) are used, essentially, in the same type of applications where solid wood is used

16.7 Future Developments

The main future developments in the thematic dealt with in this chapter are related to the need of developing selection and conformity criteria, and performance and durability standardised tests for adhesive systems to be used in the main fields of application. It is also necessary to develop non-destructive methods for assessing the quality of the bonds produced, both initial and during the working life of the structure. Given the pressing need to adopt building solutions increasingly sustainable and the environmental advantages associated with the use of adhesives in civil engineering, it is expected that the use of adhesives continues to grow in the construction industry [110, 111]. Another factor, which has significantly contributed and will increasingly contribute to this growth, lies in the fact that the adhesive producers have already begun to produce adhesives in which some components are derived from renewable sources [112, 113]. Lastly, adhesive products will have to adapt to increasingly stringent environmental requirements, regarding the toxicity of their components, and the substances that they release during cure and during their working life [114].

16.8 Standards, Regulations and Other Useful Bibliography

16.8.1 Bonding System Selection

16.8.1.1 Concrete Structures

- ACI 503.1 Standard specifications for bonding hardened concrete steel, wood, brick and other materials to hardened concrete with a multi-component epoxy adhesive.
- ACI 503.2 Standard specifications for bonding plastic concrete to hardened concrete with a multi-component epoxy adhesive.
- ACI 503.3 Standard specifications for producing a skid-resistant surface on concrete by the use of a multi-component epoxy system.
- ACI 503.4 Standard specifications for repairing concrete with epoxy mortars.
- ACI 503.5R Guide for the selection of polymer adhesives in concrete.
- ACI 503.7 Specification for crack repair by epoxy injection.
- ACI 548.E Standard specifications for bonding hardened concrete steel, wood, brick and other materials to hardened concrete with a multi-component epoxy adhesive.
- ACI 548.F Specification for bonding plastic concrete to hardened concrete with a multi-component epoxy adhesive.
- ASTM C1059/C1059M Standard specification for latex agents for bonding fresh to hardened concrete.
- ASTM C881/C881M Standard specification for epoxy-resin-base bonding systems for concrete.
- EN 1799 Products and systems for the protection and repair of concrete structures. Test methods. Tests to measure the suitability of structural bonding agents for application to concrete surface.
- ICC-ES AC308 Acceptance criteria for post-installed adhesive anchors in concrete elements.

16.8.1.2 Timber Structures

- ASTM D2559 Standard specification for adhesives for structural laminated wood products for use under exterior (wet use) exposure conditions.
- EN 301 Adhesives, phenolic and aminoplastic, for load-bearing timber structures: classification and performance requirements.
- EN 386 Bonding laminated timber. Performance requirements and minimum production requirements.
- EN 12436 Adhesives for load-bearing timber structures. Casein adhesives. Classification and performance requirements.
- EN 14080 Timber structures. Bonding laminated timber and bonding solid timber. Requirements.

- EN 14374 Timber structures. Structural laminated veneer lumber (LVL). Requirements.
- EN 15425 Adhesives. One component polyurethane for load bearing timber structures. Classification and performance requirements.
- EN 15497 Finger jointed structural timber. Performance requirements and minimum production requirements.
- ISO 20152 Timber structures. Bond performance of adhesives.
  - Part 1: Basic requirements.
  - Part 2: Additional requirements.
  - Part 3: Use of alternative species for bond tests.
- ISO 22390 Timber structures. Laminated veneer lumber (LVL). Structural properties.
- DD CEN/TS 12872 Wood-based panels. Guidance on the use of load-bearing boards in floors, walls and roofs.

16.8.1.3 Metal Structures

- EN 15190 Structural adhesives. Test methods for assessing long-term durability of bonded metallic structures.
- Petrie, E. M., *Handbook of Adhesives & Sealants*, 1st ed., McGraw-Hill, 1999.

16.8.1.4 General Applications

- *Henkel Industrial Solutions Selector Guide. Adhesives, Sealants, Metal Pretreatments, Coatings, Cleaners and Metalworking Fluids*. Henkel Corporation: Madison Heights, MI, 2009.
- Hurley, S. A., «Use of epoxy, polyester and similar reactive polymers. Volume 2: Specification and use of the materials», *Construction Industry Research and Information Association*, CIRIA Project Report 78: London, 2000.
- Hurley, S. A., «Use of epoxy, polyester and similar reactive polymers. Volume 3: Materials technology», *Construction Industry Research and Information Association*, CIRIA Project Report 79: London, 2000.
- ICC-ES AC58 Acceptance Criteria for Adhesive Anchors in Masonry Elements.
- ISO 17194 Structural adhesives. A standard database of properties.
- EN 15274 General purpose adhesives for structural assembly. Requirements and test methods.

16.8.2 Bonded Connection Design

16.8.2.1 Concrete Structures

- «Bond of reinforcement in concrete», *Fédération Internationale du Béton*, FIB Bulletin No. 10, 2000.
- «Externally bonded FRP reinforcement for RC structures», *Fédération Internationale du Béton*, FIB Bulletin No. 14, 2001.
- «Guide to the Structural Use of Adhesives», *The Institution of Structural Engineers* (IStructE). SETO: London, 1999.

- «Management, maintenance and strengthening of concrete structures», *Fédé ration Internationale du Béton*, FIB Bulletin No. 17, 2002.
- «Retrofitting of concrete structures by externally bonded FRPs, with emphasis on seismic applications», *Fédération Internationale du Béton*, FIB Bulletin No. 35, 2006.
- ACI 318 Building Code Requirements for Structural Concrete and Commentary.
- Bank, L. C., *Composites for Construction: Structural Design with FRP Materials*. John Wiley & Sons: Hoboken, 2006.
- DD CEN/TS 1992-4-5 Design of fastenings for use in concrete. Post-installed fasteners. Chemical systems.
- Mays, G. and Hutchinson, A. R., *Adhesives in Civil Engineering*, 1st ed., Cambridge University Press: Cambridge, 1992.

16.8.2.2 Timber Structures

- ASTM D7199 Standard practice for establishing characteristic values for reinforced bonding laminated timber (glulam) beams using mechanics-based models.
- Blass, H. J., Aune, P., Choo, B. S., Gorlacher, R., Griffith, D. R., Hilson, B. O., Racher, P. and Steck, G. (Eds.), *Timber Engineering STEP 1: Basis of Design, Material Properties, Structural Components and Joints*. Centrum Hout: Almere, the Netherlands, 1995.
- Blass, H. J., Aune, P., Choo, B. S., Gorlacher, R., Griffith, D. R., Hilson, B. O., Racher, P. and Steck, G. (Eds.), *Timber Engineering STEP 2: Design, Details and Structural Systems*, 1st ed., Centrum Hout: Almere, the Netherlands, 1995.
- *Composite local reinforcement for timber structures—COLORETIM*, Cooperative Research Project FAIR-CT98-9548, 2001.
- *Bonding-in rods for timber structures—GIROD*, European Commission Research Directorates General (CRAFT) Cooperative Research FP4, Project reference SMT4972199, 2001.
- «Guide to the Structural Use of Adhesives», *The Institution of Structural Engineers* (IStructE). SETO: London, 1999.
- EN 1995-1-1 Eurocode 5. Design of timber structures. General. Common rules and rules for buildings.
- EN 1995-1-2 Eurocode 5. Design of timber structures. General. Structural fire design.
- EN 1995-2 Eurocode 5: Design of timber structures. Bridges.

16.8.2.3 Metal Structures

- «Guide to the Structural Use of Adhesives», *The Institution of Structural Engineers* (IStructE). SETO: London, 1999.
- Mays, G. and Hutchinson, A. R., *Adhesives in Civil Engineering*, 1st ed., Cambridge University Press: Cambridge, 1992.

16.8.2.4 General Applications

- Clarke, J. L. (Ed.), *Structural Design of Polymer Composites: EUROCOMP Design Code and Handbook*, 1st ed., E & FN Spon: London, 1996.

16.8.3 Surface Preparation

16.8.3.1 Bibliographical References

- Adams, R. D., Comyn, J. and Wake, W. C., *Structural Adhesive Joints in Engineering,* 2nd ed., Springer: London, 1997.
- Broughton, J. G. and Custódio, J., «Understanding timber structural connection systems», in *ICE Manual of Construction Materials*, vol. 2, Forde, M. C. (Ed.), Thomas Telford Ltd: London, 2009.
- Ebnesajjad, S. (Ed.), *Adhesives Technology Handbook*, 2nd ed., William Andrew Publishing: New York, 2008.
- Machado, J. S., Cruz, H., Custódio, J., Palma, P. and Dias, A., *Avaliação, Conservação e Reforço de Estruturas de Madeira*, Machado, J. S. (ed.). Verlag Dashöfer: Lisboa, 2009.
- Mays, G. and Hutchinson, A. R., *Adhesives in Civil Engineering,* 1st ed., Cambridge University Press: Cambridge, 1992.
- Petrie, E. M., *Handbook of Adhesives & Sealants,* 1st ed., McGraw-Hill, 1999.
- Pocius, A. V., *Adhesion and Adhesives Technology: An Introduction,* 2nd ed., Hanser Gardner Publications: Cincinnati, 2002.

16.8.3.2 Standards

- ASTM C1583/C1583M Standard test method for tensile strength of concrete surfaces and the bond strength or tensile strength of concrete repair and overlay materials by direct tension (pull-off method).
- ASTM D2093 Standard practice for preparation of surfaces of plastics prior to adhesive bonding.
- ASTM D2651 Standard guide for preparation of metal surfaces for adhesive bonding.
- ASTM D5295 Standard guide for preparation of concrete surfaces for adhered (bonded) membrane waterproofing systems.
- EN 13887 Structural adhesives. Guidelines for surface preparation of metals and plastics prior to adhesive bonding.
- EN ISO 8504-1 Preparation of steel substrates before application of paints and related products. Surface preparation methods. General principles.
- EN ISO 8504-2 Preparation of steel substrates before application of paints and related products. Surface preparation methods. Abrasive blast cleaning.
- EN ISO 8504-3 Preparation of steel substrates before application of paints and related products. Surface preparation methods. Hand- and power-tool cleaning.
- ISO 17212 Structural adhesives. Guidelines for the surface preparation of metals and plastics prior to adhesive bonding.
- ISO 27831-1 Metallic and other inorganic coatings. Cleaning and preparation of metal surfaces. Ferrous metals and alloys.

- ISO 27831-2 Metallic and other inorganic coatings. Cleaning and preparation of metal surfaces. Non-ferrous metals and alloys.

16.8.4 Process Control

16.8.4.1 Bibliographical References

- «Design Manual for Roads and Bridges. Volume 3: Highway Structures: Inspection & Maintenance. Section 16.3: Repair and Strengthening. Part 1: BA 30/94 Strengthening of Concrete Highway Structures Using Externally Bonded Plates». Highways Agency, UK: London, 1994.
- «Guide to the Structural Use of Adhesives», *The Institution of Structural Engineers* (IStructE). SETO: London, 1999.
- «Low Intrusion Conservation Systems for Timber Structures—LICONS (http://www.licons.org/)», European Commission Research Directorates General (CRAFT) Cooperative Research FP5, Project reference EVK4-CT-2002-30008, 2005.
- Dunky, M., Källender, B., Properzi, M., Richter, K. and Leemput, M. V. (eds.), *Core document of the COST Action E34—Bonding of Timber*, in Lignovisionen, Special ed., University of Natural Resources and Applied Life Sciences: Vienna, 2008.
- Ebnesajjad, S. (Ed.), *Adhesives Technology Handbook*, 2nd ed., William Andrew Publishing: New York, 2008.
- Mays, G. and Hutchinson, A. R., *Adhesives in Civil Engineering,* 1st ed., Cambridge University Press: Cambridge, 1992.
- *Repair of Concrete Structures to EN 1504. A guide for renovation of concrete structures—repair materials and systems according to the EN 1504 series*, 1st ed., Elsevier Butterworth-Heinemann: Oxford, 2004.
- «Repair of concrete structures with reference to BS EN 1504 (Technical Report 69)». *The Concrete Society: Crowthorne*, Berkshire, UK, 2009.

16.8.4.2 Standards

- EN 1504 Products and systems for the protection and repair of concrete structures. Definitions, requirements, quality control and evaluation of conformity.
  - Part 1: Definitions.
  - Part 2: Surface protection systems for concrete.
  - Part 3: Structural and non-structural repair.
  - Part 4: Structural bonding.
  - Part 5: Concrete injection.
  - Part 6: Anchoring of reinforcing steel bar.
  - Part 7: Reinforcement corrosion protection.
  - Part 8: Quality control and evaluation of conformity.
  - Part 9: General principles for the use of products and systems.
  - Part 10: Site application of products and systems and quality control of the works.

16.8.5 Performance and Durability

16.8.5.1 Bibliographical References

- Adams, R. D., Comyn, J. and Wake, W. C., *Structural Adhesive Joints in Engineering,* 2nd ed., Springer: London, 1997.
- Comyn, J., *Adhesion Science*, 1st ed., Royal Society of Chemistry: Cambridge, 1997.
- Custódio, J., Broughton, J. and Cruz, H., «A review of factors influencing the durability of structural bonded timber joints». *International Journal of Adhesion and Adhesives*, vol. 29, (2), pp. 173-185, 2009.
- Ebnesajjad, S. (Ed.), *Adhesives Technology Handbook*, 2nd ed., William Andrew Publishing: New York, 2008.
- Kinloch, A. J. (Ed.), *Durability of Structural Adhesives*, 1st ed., Applied Science Publishers Ltd.: Barking, UK, 1983.
- Kinloch, A. J., *Adhesion and Adhesives: Science and Technology*, 1st ed., Chapman & Hall: London, 1987.
- Mays, G. and Hutchinson, A. R., *Adhesives in Civil Engineering,* 1st ed., Cambridge University Press: Cambridge, 1992.
- Petrie, E. M., *Handbook of Adhesives & Sealants*, 1st ed., McGraw-Hill, 1999.
- Pizzi, A. and Mittal, K. L. (eds.), *Handbook of Adhesive Technology*, 2nd ed., Marcel Dekker: New York, 2003.

16.8.5.2 Standards

- ASTM E1512 Standard test methods for testing bond performance of bonded anchors.
- EN 302 Adhesives for load-bearing timber structures. Test methods.
  - Part 1: Determination of bond strength in longitudinal tensile shear strength.
  - Part 2: Determination of resistance to delamination.
- EN 408 Timber structures. Structural timber and bonding laminated timber. Determination of some physical and mechanical properties.
- EN 1193 Timber structures. Structural timber and bonding laminated timber. Determination of shear strength and mechanical properties perpendicular to the grain.
- EN 1195 Timber structures. Test methods. Performance of structural floor decking.
- EN 1544 Products and systems for the protection and repair of concrete structures. Test methods. Determination of creep under sustained tensile load for synthetic resin products (PC) for the anchoring of reinforcing bars.
- EN 1799 Products and systems for the protection and repair of concrete structures. Test methods. Tests to measure the suitability of structural bonding agents for application to concrete surface.
- EN 1881 Products and systems for the protection and repair of concrete structures. Test methods. Testing of anchoring products by the pull-out method.
- EN ISO 9664 Adhesives. Test methods for fatigue properties of structural adhesives in tensile shear (ISO 9664).

- EN 12188 Products and systems for the protection and repair of concrete structures. Test methods. Determination of adhesion steel-to-steel for characterization of structural bonding agents
- EN 12614 Products and systems for the protection and repair of concrete structures. Test methods. Determination of glass transition temperatures of polymers.
- EN 12617 Products and systems for the protection and repair of concrete structures. Test methods.
  - Part 1: Determination of linear shrinkage for polymers and surface protection systems (SPS).
  - Part 2: Shrinkage of crack injection products based on polymer binder: volumetric shrinkage.
  - Part 3: Determination of early age linear shrinkage for structural bonding agents.
  - Part 4: Determination of shrinkage and expansion.
- EN 12618 Products and systems for the protection and repair of concrete structures. Test methods.
  - Part 1: Adhesion and elongation capacity of injection products with limited ductility.
  - Part 2: Determination of the adhesion of injection products, with or without thermal cycling. Adhesion by tensile bond strength.
  - Part 3: Determination of the adhesion of injection products, with or without thermal cycling. Slant shear method.
- EN 13584 Products and systems for the protection and repair of concrete structures. Test methods. Determination of creep in compression for repair products.
- EN 13733 Products and systems for the protection and repair of concrete structures. Test methods. Determination of the durability of structural bonding agents.
- EN 13894 Products and systems for the protection and repair of concrete structures. Test methods.
  - Part 1: Determination of fatigue under dynamic loading. During curing.
  - Part 2: Determination of fatigue under dynamic loading. After hardening.
- EN 14258 Structural adhesives. Mechanical behaviour of bonded joints subjected to short and long terms exposure at specified conditions of temperature.
- EN 14444 Structural adhesives. Qualitative assessment of durability of bonded assemblies. Wedge rupture test.
- EN ISO 11343 Adhesives. Determination of dynamic resistance to cleavage of high-strength adhesive bonds under impact conditions. Wedge impact method.
- EN 14869 Structural adhesives. Determination of shear behaviour of structural bonds.
  - Part 1: Torsion test method using butt-bonded hollow cylinders.
  - Part 2: Thick adherends shear test.

- EN 15190 Structural adhesives. Test methods for assessing long term durability of bonded metallic structures.
- EN 15416 Adhesives for load bearing timber structures other than phenolic and aminoplastic. Test methods.
  - Part 2: Static load test of multiple bondline specimens in compression shear.
  - Part 3: Creep deformation test at cyclic climate conditions with specimens loaded in bending shear.
- ISO 19993 Timber structures. Bonding laminated timber. Face and edge joint cleavage test.
- ISO 16572 Timber structures. Wood-based panels. Test methods for structural properties.

16.8.6 Applications

16.8.6.1 Bibliographical References

- *Concrete Repair Manual*, 4th ed., American Concrete Institute (ACI)—International Concrete Repair Institute (ICRI), 2013.
- Appleton, J. A. S., *Reabilitação de Edifícios Antigos—Patologias e tecnologias de intervenção*, 1ª ed., Edições Orion: Amadora, 2003.
- Appleton, J. G., *Reabilitação de Edifícios «Gaioleiros»—Um Quarteirão em Lisboa*, 1ª ed., Edições Orion: Amadora, 2005.
- Bijen, J., *Durability of Engineering Structures: Design, Repair and Maintenance*, 1st ed., Woodhead Publishing Ltd and CRC Press LLC: Abington and Boca Raton, 2003.
- Cóias e Silva, V., *Reabilitação Estrutural de Edifícios Antigos. Alvenaria-Madeira. Técnicas pouco Intrusivas*, 2nd ed., Argumentum: Lisboa, 2007.
- Emmons, P. H., *Concrete Repair and Maintenance Illustrated: Problem Analysis, Repair Strategy, Techniques*. R.S. Means Company: Kingston, MA, 1994.
- Forde, M. C. (ed.), *ICE Manual of Construction Materials*. «Fundamentals and Theory; Concrete; Asphalts in Road Construction; Masonry», vol. 1. Thomas Telford: London, 2009.
- Forde, M. C. (Ed.), *ICE Manual of Construction Materials*. «Metals and Alloys; Polymers; Polymer Fibre Composites in Civil Engineering; Timber; Glass; non-Conventional Materials», vol. 2. Thomas Telford: London, 2009.
- Hurley, S. A., «Use of epoxy, polyester and similar reactive polymers. Volume 1—materials and their practical applications», *Construction Industry Research and Information Association*, CIRIA Project Report 79: London, 2000.
- Irfan, M. H., «Chemistry and Technology of Thermosetting Polymers in Construction Applications». *Kluwer Academic Publishers: Dordrecht*, The Netherlands, 1998.
- Machado, J. S., Cruz, H., Custódio, J., Palma, P. and Dias, A., *Avaliação, Conservação e Reforço de Estruturas de Madeira (Evaluation, conservation and reinforcement of timber structures)*, Machado, J. S. (ed.). Verlag Dashöfer: Lisboa, 2009.

- Mays, G. and Hutchinson, A. R., *Adhesives in Civil Engineering,* 1st ed., Cambridge University Press: Cambridge, 1992.
- Perkins, P. H., *Repair, Protection and Waterproofing of Concrete Structures*, 3rd ed., E & FN Spon: London, 1997.
- Radomski, W., «Bridge Rehabilitation». *Imperial College Press*: London, 2002.
- Shi, C. and Mo, Y. L. (Eds.), «High-Performance Construction Materials: Science and Applications», in *Engineering Materials for Technological Needs*, vol. 1. World Scientific Publishing Company: Singapore, 2008.
- Bai, J. (Ed.), *Advanced fibre-reinforced polymer (FRP) composites for structural applications*, Woodhead Publishing: Cambridge, 2013.

16.8.6.2 Specifications

- ACI 503.2 Standard specification for bonding plastic concrete to hardened concrete with a multi-component epoxy adhesive.
- ACI 503.3 Specification for producing a skid-resistant surface on concrete by the use of epoxy and aggregate.
- ACI 503.4 Standard specification for repairing concrete with epoxy mortars.
- ACI 503.5R Guide for the selection of polymer adhesives with concrete.
- ACI 503.7 Specification for Crack Repair by Epoxy Injection.
- ACI 546.2R Guide to underwater repair of concrete.
- ACI 546.3R Guide for the selection of materials for the repair of concrete.
- ACI 546R Concrete repair guide.
- ACI 548.11R Guide for application of epoxy and latex adhesives for bonding freshly mixed and hardened concretes.
- ACI 548.12 Specification for bonding hardened concrete and steel to hardened concrete with an epoxy adhesive.
- ACI 548.F Specification for Bonding Fresh Concrete to Hardened Concrete with a Multi-Component Epoxy Adhesive.
- ACI 548.G Specification for Repairing Concrete with Epoxy Mortars.
- ACI 548.HR Guide for the application of epoxy and latex adhesives for bonding fresh to hardened concrete.

Acknowledgments The author wishes to acknowledge the courtesy of Rotafix Ltd. (Rotafix House, Hennoyadd Road, Abercrave, Swansea, SA9 1UR, United Kingdom) (http://rotafix.co.uk/) for supplying the images of Figure 16.3.

References

1. Kisser JG, Ylinen A, Freudenberg K, Kollmann FFP, Liese W, Thunell B, Winkelmann HG, Côté WA, Koch P, Marian JE, Stamm AJ (1967) History of wood science. Wood Sci Technol 1(3):161–190
2. Pizzi A, Mittal KL (2003) Handbook of adhesive technology, 2nd edn. Marcel Dekker, New York
3. Petrie EM (1999) Handbook of adhesives and sealants, 1st edn. McGraw-Hill, New York

4. (2005) Construction and Strengthening of GFRP Structures with Sikadur® Structural Adhesives. In: Sika at work—corporate construction no. 04. Sika Services AG, Zürich
5. Rotafix Ltd. Case Studies. The Tourand Creek Bridge, Winnipeg, Manitoba, Canada. Rotafix Ltd., Abercraf, Swansea. http://rotafix.co.uk/casestudies/tourand/. Accessed 5 March 2014
6. NP 3672:1990 Colas. Terminologia. Definições. Instituto Português da Qualidade, I.P. (IPQ), Caparica
7. ASTM D 907-11a Standard terminology of adhesives. ASTM International, West Conshohocken, PA
8. EN ISO 472:2001 Plastics. Vocabulary. European Committee for Standardization (CEN), Brussels
9. EN 923:2005 + A1:2008 Adhesives. Terms and definitions. European Committee for Standardization (CEN), Brussels
10. Adams RD, Comyn J, Wake WC (1997) Structural adhesive joints in engineering, 2nd edn. Springer, London
11. Pocius AV (2002) Adhesion and adhesives technology: an introduction, 2nd edn. Hanser Gardner Publications, Cincinnati
12. Kinloch AJ (1987) Adhesion and adhesives: science and technology, 1st edn. Chapman & Hall, London
13. Mays G, Hutchinson AR (1992) Adhesives in civil engineering, 1st edn. Cambridge University Press, Cambridge
14. (1999) Wood handbook: wood as an engineering material. General technical report FPL-GTR-113. United States Department of Agriculture, Forest Service, Forest Products Laboratory, Madison, WI
15. Unger A, Schniewind A, Unger W (2001) Conservation of wood artifacts: a handbook. Springer, New York
16. Newey C, Boff R, Daniels V, Pascoe M, Tennant N (1992) Science for conservators: adhesives and coatings. In: Wilks H (ed) Conservation science teaching series, vol 3, The Conservation Unit Museums and Galleries Commission ed. Routledge, London
17. Moncrieff A, Weaver G (1992) Science for conservators: cleaning. In: Wilks H (ed) Conservation science teaching series, vol 2, The conservation unit museums and galleries commission ed. London, Routledge
18. Moncrieff A, Weaver G (1992) Science for conservators: an introduction to materials. In: Wilks H (ed) Conservation science teaching series, vol 1, The conservation unit museums and galleries commission ed. Routledge, London
19. Horie CV (1987) Materials for conservation: organic consolidants, adhesives and coatings. In: Rees-Jones SG, Linstrum D (eds) Conservation and museology series, vol. Butterworths, Oxford
20. Hogan J, Arthur J (1952) Cottonseed and peanut meal glues. Resistance of plywood bonds to chemical reagents. J Am Oil Chem Soc 29(1):16–18
21. Ebnesajjad S (2008) Adhesives technology handbook, 2nd edn. William Andrew Publishing, New York
22. Comyn J (1997) Adhesion science, 1st edn. Royal Society of Chemistry, Cambridge
23. Broughton JG, Custódio J (2009) Understanding timber structural connection systems. In: Forde MC (ed) ICE manual of construction materials, vol 2. Thomas Telford Ltd, London
24. Smith RW (2002) Adhesives from natural sources—pre-history to the present. In: Workshop on adhesives from natural sources. Co-sponsored by Adhesives Age Magazine and The Adhesive and Sealant Council, Cleveland, OH
25. Jones RG, Wilks ES, Metanomski WV, Kahovec J, Hess M, Stepto R, Kitayama T (2009) Compendium of polymer terminology and nomenclature. International Union of Pure and Applied Chemistry (IUPAC) recommendations 2008. The Royal Society of Chemistry, Cambridge
26. Elias H-G (2003) An introduction to plastics, 2nd edn. Weinheim, Wiley-VCH
27. Whelan T (1994) Polymer technology dictionary, 1st edn. Chapman & Hall, London

28. ASC (2006) Standard definitions of terms relating to adhesives. The Adhesive and Sealant Council, Bethesda, MD
29. BS EN 1995-1-1:2004 + A1:2008 Eurocode 5. Design of timber structures. General. Common rules and rules for buildings. British Standards Institution (BSI), London
30. EN 301:2006 Adhesives, phenolic and aminoplastic, for load-bearing timber structures. Classification and performance requirements. European Committee for Standardization (CEN), Brussels
31. ASTM D 4800-94 (Reapproved 2011) Standard guide for classifying and specifying adhesives. ASTM International, West Conshohocken, PA
32. ASTM C 881/C 881M-13 Standard specification for epoxy-resin-base bonding systems for concrete. ASTM International, West Conshohocken, PA
33. Conner AH (2001) Wood: adhesives. In: Buschow KHJ (ed) Encyclopedia of materials: science and technology, vol 10. Elsevier Science, Oxford
34. Dunky M, Pizzi A (2002) Wood adhesives. In: Pocius AV, Chaudhury M (eds) Surfaces, chemistry and applications: adhesion science and engineering, 2. Elsevier Science, Amsterdam
35. Sellers T, McSween JR, Nearn WT (1988) Gluing of Eastern Hardwoods: a review. General technical report SO-71. United States Department of Agriculture, Forest Service, Southern Forest Experimental Station, New Orleans
36. Hurley SA (2000) Use of epoxy, polyester and similar reactive polymers. Vol 1: Materials and their practical applications. Construction Industry Research and Information Association, London, CIRIA Publication C537
37. Hurley SA (2000) Use of epoxy, polyester and similar reactive polymers. Vol 2: Specification and use of the materials. Construction Industry Research and Information Association, London, CIRIA Project Report 78
38. Hurley SA (2000) Use of epoxy, polyester and similar reactive polymers. Vol 3: Materials technology. Construction Industry Research and Information Association, London, CIRIA Project Report 79
39. IStructE (1999) Guide to the structural use of adhesives. The Institution of Structural Engineers (IStructE), London
40. ACI (1992) ACI 503.5R-92 (Reapproved 2003): Guide for the selection of polymer adhesives in concrete. American Concrete Institute (ACI), Farmington Hills, MI
41. Marra AA (1992) Technology of wood bonding—principles in practice. Van Nostrand Reinhold, New York
42. Packham DE (2005) Handbook of adhesion, 2nd edn. Wiley, Chichester
43. Rowell RM (2005) Handbook of wood chemistry and wood composites. CRC Press, Boca Raton
44. Allen KW (2003) At forty cometh understanding. A review of some basics of adhesion over the past four decades. Int J Adh Adhes 23(2):87–93
45. Gardner DJ (2005) Adhesion mechanisms of durable wood adhesive bonds. In: Stokke DD, Groom LH (eds) Characterization of the cellulosic cell wall, 1st edn. Blackwell Publishing, Grand Lake, CO
46. McBain JW, Hopkins DG (1925) On adhesives and adhesive action. J Phys Chem 29 (2):188–204
47. Evans JRG, Packham DE (1979) Adhesion of polyethylene to metals: the role of surface topography. J Adh 10(3):177–191
48. Jennings CW (1972) Surface roughness and bond strength of adhesives. J Adh 4(1):25–38
49. Lee LH (1991) Adhesive bonding. Plenum Press, New York
50. Wake WC (1976) Adhesion and the formulation of adhesives. Applied Science Publishers, London
51. Evans JR, Packham DE (1977) Adhesion. In: Allen KW (ed), vol 1. Applied Science Publishers, London

52. Packham DE (1981) Developments in adhesives. In: Kinloch AJ (ed), vol 2. Applied Science Publishers, London
53. Packham DE (1983) Developments in adhesives. In: Mittal KL (ed). Plenum Press, New York
54. Adhesion theory—mechanical interlocking. SpecialChem S.A., Paris. http://www.specialchem4adhesives.com/resources/adhesionguide/index.aspx?id=theory4. Accessed 15 Feb 2010
55. Sharpe Louis H, Schonhorn H (1964) Surface energetics, adhesion, and adhesive joints. In: Robert F. Gould (ed), Contact angle, wettability, and adhesion. Advances in chemistry. American Chemical Society, Washington, DC
56. Allara DL, Fowkes FM, Noolandi J, Rubloff GW, Tirrell MV (1986) Bonding and adhesion of polymer interfaces. Mater Sci Eng 83(2):213–226
57. Fowkes FM (1987) Role of acid-base interfacial bonding in adhesion. J Adh Sci Technol 1 (1):7–27
58. Kinloch AJ (1979) Interfacial fracture mechanical aspects of adhesive bonded joints—a review. J Adh 10(3):193–219
59. Gledhill RA, Kinloch AJ, Shaw SJ (1980) A model for predicting joint durability. J Adh 11 (1):3–15
60. Kinloch AJ (1980) Review. The science of adhesion. Part 1. Surface and interfacial aspects. J Mater Sci 15(9):2141–2166
61. Adhesion theory—adsorption. SpecialChem S.A., Paris. http://www.specialchem4adhesives.com/resources/adhesionguide/index.aspx?id=theory2. Accessed 15 Feb 2010
62. Plueddemann EP (1992) Silanes and other coupling agents. In: Mittal KL (ed) Reminiscing on silane coupling agents, vol 1. Zeist, VSP
63. Plueddemann EP (1982) Silanes coupling agents. Plenum Press, New York
64. Lee LH (1991) Fundamentals of adhesion. Plenum Press, New York
65. Ho PS, Han PO, Bartha JW, Rubloff GW, LeGoues FK, Silverman BD (1985) Chemical bonding and reaction at metal/polymer interfaces. J Vac Sci Technol A Vac Surf Films 3 (3):739–710
66. Haight R, White RC, Silverman BD, Ho PS (1988) Complex formation and growth at the Cr– and Cu–polyimide interface. J Vac Sci Technol A Vac Surf Films 6(4):2188–2199
67. Adhesion theory—chemisorption. SpecialChem S.A., Paris. http://www.specialchem4adhesives.com/resources/adhesionguide/index.aspx?id=theory3. Accessed 15 Feb 2010
68. Deryaguin BV (1955) Problems of adhesion. Research 8:70
69. Krupp H, Schnabel W (1973) Light-modulated electrostatic double layer adhesion. J Adh 5 (4):269–277
70. von Harrach HG, Chapman BN (1972) Charge effects in thin film adhesion. Thin Solid Films 13(1):157–161
71. Roberts AD (1977) Surface charge contribution in rubber adhesion and friction. J Phys D Appl Phys 10(13):1801
72. Possart W (1988) Experimental and theoretical description of the electrostatic component of adhesion at polymer/metal contacts. International Journal of Adhesion and Adhesives 8(2):73
73. Adhesion theory—electrostatic. SpecialChem S.A., Paris. http://www.specialchem4adhesives.com/resources/adhesionguide/index.aspx?id=theory6. Accessed 15 Feb 2010
74. Voiutskii SS (1963) Autohesion and adhesion of high polymers. Wiley-Interscience, New York
75. Vasenin RM (1969) Adhesion: fundamentals and practice (Report of the International Conference on Adhesion held at the University of Nottingham, England, 20-22 September 1966 by the Ministry of Technology, United Kingdom). Maclaren and Sons, London
76. Klein J (1979) The self-diffusion of polymers. Contemp Phys 20(6):611–629
77. Edwards SF, Grant JWV (1973) The effect of entanglements on the viscosity of a polymer melt. J Phys A Math Nuclear Gen 6(8):1186

78. Brochard F, Gennes PGD (1986) Polymer-polymer interdiffusion. EPL (Europhys Lett) 1 (5):221
79. Wu S, Chuang H-K, Han CD (1986) Diffuse interface between polymers: structure and kinetics. J Polym Sci B 24(1):143–159
80. Adhesion theory—diffusion. SpecialChem S.A., Paris. http://www.specialchem4adhesives.com/resources/adhesionguide/index.aspx?id=theory5. Accessed 15 Feb 2010
81. Bikerman JJ (1961) The science of adhesive joints. Academic, New York
82. Bascom W, Timmons C, Jones R (1975) Apparent interfacial failure in mixed-mode adhesive fracture. J Mater Sci 10(6):1037–1048
83. Good RJ (1972) Theory of “cohesive” vs “adhesive” separation in an adhering system. J Adh 4(2):133–154
84. Schultz J (1992) Effect of orientation and organization of polymers at interfaces on adhesive strength. J Adh 37(1–3):73–81
85. Nardin M, Maliki AE, Schultz J (1993) Interface and interphase in carbon fibre-styrene butadiene rubber (SBR) composites. J Adh 40(2–4):93–106
86. Schultz J, Carré A, Mazeau C (1984) Formation and rupture of grafted polyethylene/aluminium interfaces. Int J Adh Adhes 4(4):163–168
87. Schultz J, Lavielle L, Carre A, Comien P (1989) Surface properties and adhesion mechanisms of graft polypropylenes. J Mater Sci 24(12):4363–4369
88. Nardin M, Asloun EM, Muller F, Schultz J (1991) Study of the carbon fiber–poly(ether–ether–ketone) (PEEK) interfaces, 3: influence and properties of interphases. Polym Adv Technol 2(4):161–169
89. Adams RD, Wake WC (1984) Structural adhesive joints in engineering. Elsevier Applied Science, London
90. Machado JS, Cruz H, Custódio J, Palma P, Dias A (2009) Avaliação, Conservação e Reforço de Estruturas de Madeira (Evaluation, conservation and reinforcement of timber structures). In: Machado JS (ed). Dashöfer, Lisboa
91. Custódio J, Broughton J, Cruz H, Hutchinson A (2008) A review of adhesion promotion techniques for solid timber substrates. J Adh 84(6):502–529
92. Custódio J, Broughton J, Cruz H (2009) A review of factors influencing the durability of structural bonded timber joints. Int J Adh Adhes 29(2):173–185
93. Custódio J, Broughton J, Cruz H, Winfield P (2009) Activation of timber surfaces by flame and corona treatments to improve adhesion. Int J Adh Adhes 29(2):167–172
94. Cruz H, Custódio J (2010) Adhesives for on-site rehabilitation of timber structures. J Adh Sci Technol 24(8):1473–1499
95. Custódio J, Broughton J, Cruz H (2011) Evaluation of adhesion promotion techniques for structural bonded timber joints. J Adh 87(4):331–352
96. Custódio J, Broughton J, Cruz H (2011) Rehabilitation of timber structures—preparation and environmental service condition effects on the bulk performance of epoxy adhesives. Construct Build Mater 25(8):3570–3582
97. Custódio J, Broughton J, Cruz H (2012) Rehabilitation of timber structures—novel test method to assess the performance and durability of bonded-in rod connections. Mater Struct 45(1–2):199–221
98. Henkel (2009) Henkel industrial solutions selector guide. Adhesives, sealants, metal pretreatments, coatings, cleaners and metalworking fluids. Henkel Corporation: Madison Heights, MI
99. The adhesives design toolkit. http://www.adhesivestoolkit.com. Accessed 29 Jan 2010
100. Adhesion selector. SpecialChem S.A., Paris. http://www.specialchem4adhesives.com/resources/adhesionguide/selector.aspx. Accessed 15 Jan 2010
101. (2002) EN 1990:2002 + A1:2005 Eurocode. Basis of structural design. European Committee for Standardization (CEN), Brussels
102. Cruz H, Custódio J, Nascimento J, Empis M. (2004) Execução e controlo de qualidade da reparação de estruturas de madeira com colas epoxídicas e FRPs (Execution and quality

control of timber structures repair with epoxy adhesives and FRPs). In: 1° Congresso Ibérico sobre A madeira na construção—CIMAD'04 (1st Iberian Congress on Timber in Construction), Guimarães, Portugal
103. Kinloch AJ (1983) Durability of structural adhesives, 1st edn. Applied Science Publishers Ltd., Barking
104. ACI (1993) ACI 503R-93 (Reapproved 2008): use of epoxy compounds with concrete. American Concrete Institute (ACI), Farmington Hills, MI
105. Cóias e Silva V. (2007) Reabilitação Estrutural de Edifícios Antigos. Alvenaria-Madeira. Técnicas pouco Intrusivas, 2nd edn. Argumentum, Lisboa
106. Appleton JAS (2003) Reabilitação de Edifícios Antigos—Patologias e tecnologias de intervenção, 1ªth edn. Edições Orion, Amadora
107. Perkins PH (1997) Repair, protection and waterproofing of concrete structures, 3rd edn. E & FN Spon, London
108. Danish Standards Association (2004) Repair of concrete structures to EN 1504. A guide for renovation of concrete structures—repair materials and systems according to the EN 1504 series, 1st edn. Elsevier Butterworth-Heinemann, Oxford
109. Akovali G (2005) Polymers in construction. Rapra Technology, Shawbury
110. Heinrich H (2009) Going Green—in the Adhesives and Sealants Industry: a major concern in Europe. SpecialChem4Adhesives (April 1)
111. Ferguson LT (2005) Green bonds. SpecialChem (November, 1)
112. Shen L, Haufe J, Patel MK (2009) Product overview and market projection of emerging bio-based plastics. Final report PRO-BIP 2009, Utrecht University, Utrecht
113. Wegner J (2004) The future of adhesives and sealants seen from a European perspective. In: 6th World adhesives conference—innovation and future of the world adhesives industry, Beijing
114. Heitmann K (2006) REACH requirements for adhesives manufacturers and users. Adhesives and Sealants Industry magazine (November)

Organic Coatings

17

Alda Simões

Abstract

Organic coatings are the most widely used finishing for all kinds of structures. In this chapter, a brief presentation of organic coatings and of its properties is made, dealing namely with the components and their role in the coating performance, the properties of the dry coating, the degradation mechanisms and finally the specific properties for coatings designed for various substrates. The chapter is meant to provide non-experts with a general look over the world of organic coatings.

Keywords

Organic coatings • Polymeric materials • Weathering • Pigments • Binder • Curing • Adhesion • Dispersion • Pigment volume concentration • Chalking • Volatile components (of an organic coating) • ZETA potential • Acid pollutants • Gloss • Cracking

17.1 Introduction

Most objects and surfaces that surround us are covered by a finishing layer, commonly with a composition different from the base material and which in some way improves the aptitude of the object or surface to its final use. Coatings can be metallic (like galvanized steel, in which steel is coated with zinc), inorganic non-metallic (like anodized aluminium, in which the base metal undergoes chemical conversion at the surface, producing a protective layer of aluminium oxide) or organic. This last group, which includes paints and varnishes, is used in practically

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M.C. Gonçalves, F. Margarido (eds.), *Materials for Construction and Civil Engineering*, DOI 10.1007/978-3-319-08236-3_17

all types of applications, from the automotive industry, to aeronautics, to furniture or architecture.

Whatever the application, organic coatings always perform several functions:

- Protective function: the coating is a barrier that separates the surface from the outer environment, increasing its resistance to air, water, solvents (organic liquids) and chemically aggressive liquids (acid or alkaline).
- Decorative function: it is reached by means of colour, texture and brightness.
- Hygienic function: on walls and pavements, and also in other applications, such as furniture, the organic coating, by decreasing the roughness of the surface and also by changing its composition, can decrease its tendency to accumulate bacteria, dirt and other impurities, thus easing the cleaning processes.
- Impermeabilization: this is a particular case of the protective function. Organic coatings constitute a barrier to the outer environment, thus isolating the material from the outer humidity; further, they tend to fill the recessed areas or cracks on the surface, further protecting from the effects of water.

17.2 Historical Notes

Although the production and commercialization of paints as an industrial and economic activity only gained expression after the First World War, the use of paints is nearly as old as the history of mankind. The oldest remains of paint can be found in caves and date from more than 10,000 years ago. They were made simply by scribing the rock with minerals or by applying the powdered pigments. Later, these pigments were mixed with animal fat or vegetable oils, which agglutinated the particles and improved the adhesion to walls [1]. Around 8000–6000 B.C., the Egyptians used paints based on gum arabic, egg, gelatin or beeswax as binders. In particular, the paints using beeswax were applied molten and were used to protect hulls of ships; they were the first known application of paints with a protective function. It was also in ancient Egypt that many pigments were developed, both natural and synthetic, particularly the pigment known as *blue of Egypt*, made from lime, sand, copper oxide and sodium carbonate, heated and finely grounded. Around 1000–220 B.C., also the Chinese used paints (lacquer), in this case with the aim of coating furniture and houses, both internally and externally [2].

During the Middle Ages, the use of paints and varnishes became common for the protection of wooden houses, whereas during the seventeenth century decorative wooden objects coated with *oriental lacquer* became popular in Europe.

Around the middle of the nineteenth century, the advent of railway was crucial in the development of anti-corrosion paints, which consisted of one or more layers based upon lead oxide, followed by one or more layers of topcoat based on graphite and linseed oil. This system is responsible for the grey colour of many railway bridges and has proven to be good for protection against weathering in the long term, although it performs not so well in maritime or industrial environments.

Until the end of the nineteenth century, paints were usually prepared by the painters themselves, in a process that included the grinding of pigments and their dispersion in oils or varnishes using stone mills. At that time most formulations used vegetable oils, namely linseed oil.

It was only in the years 1920s and 1930s, with the advent of macromolecular chemistry, that the modern technology of polymers was started and many of the modern resins were synthetized, namely alkyd resins, chlorinated rubber, urea-formaldehyde or the vinylic and acrylic copolymers. In industrial terms, however, the impact of these new resins became relevant only after the consolidation of the chemistry of organic solvents and plasticizers, which allowed the development of commercially successful formulations. For example, systems of the highest commercial impact polyurethane and epoxy resins were developed only after the Second World War.

Organic coatings have a vast range of applications in engineering, namely in the automotive industry, which is among the largest users of paints, but also in the metalworking industries and on metal- and concrete-based structures in construction and architecture, such as bridges and buildings, just to mention a few.

17.3 Composition

A paint can be defined as a pigmented composite which, when applied as a thin layer onto an appropriate surface, can be converted after a certain time into a solid, opaque and coloured coating.

The basic components of a liquid paint are the *binder*, the *solvents* (volatile components), the *pigments* and the *additives*. Varnishes are organic coatings to which pigments are not added (with the aim of maintaining transparency), whereas some paints do not use solvents.

A paint system is usually made of two or more layers. Further to the specific functions of each layer, the use of multiple layers has the advantage of better hindering the access of water and moisture to the substrate, not just because of the increased thickness but also because the pores become discontinuous—Fig. 17.1.

17.3.1 The Binder

The binder is responsible for the cohesive forces that keep the structure and the continuity of the paint. It consists of one or more types of organic resins and the name of the family of paints is usually associated to the resin used; for example, an acrylic paint has an acrylic resin as binder, although a wide range of acrylic polymers can be used [3].

Of all the components of a paint, the binder is the only one that has to be present in every organic coating, in contrast with the other components, which can be absent from some formulations. The binder is responsible for providing the body to

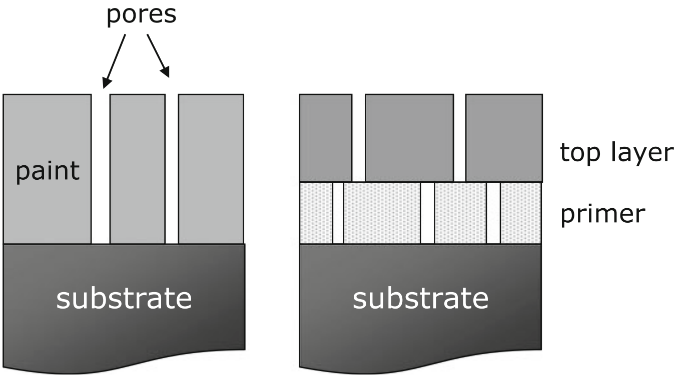

Fig. 17.1 Efect of the number of layers on the pore structure of organic coatings

the coating and also for the adhesion forces to the surface. Most binders consist of polymeric materials or macromolecules. A polymer is a molecule consisting of a repetition of many chemical structural units, bound among them through covalent bonds. The repeating unit is called a "*mer*" ("part", from the Greek). The length of the molecules (or their molecular weight), their degree of branching and the degree of cross-linking are determinant for the coating properties, in the same way as in polymeric materials.

17.3.1.1 The Processes of Curing or Drying

The terms "curing" and "drying" correspond to a set of physico-chemical transformations that occur in the transformation of a liquid paint into a cohesive, viscoelastic and adherent film. The cure can occur through several mechanisms, as described below.

Physical drying is a process in which the formation of the film results only from the evaporation of the volatile components. As the amount of solvent becomes very small, the molecules approach one another until the secondary valence forces start to act, leading to the formation of a gel and finally to a cohesive film. This process occurs generally in a short period, of a few minutes. These bonds are held by weak secondary valence forces and can usually be broken again by solvents. This is the case of cellulose lacquer, which can easily be removed by acetone or other solvents. Commonly they use nitrocellulose, ethyl cellulose or other esters of cellulose, vinyl resins—poly(vinyl acetate) and poly(vinyl chloride)—acrylic ester resins, chlorinated rubber, bitumen (tar) and some glues as binders. One example of ethyl cellulose lacquer is the spray used for hair, which quickly dries in air and is easily removed by washing.

Chemical drying is a process by which the binder molecules react with each other and thus become bound together by primary valencies. It can take place by one of two mechanisms, oxidative drying or "curing".

Oxidative drying is a polymerization process involving oxygen from air. This process is much slower than physical drying but it can be accelerated by substances that work as catalysts, generally called "driers", like some organic salts of lead, manganese and cobalt, soluble in the binder. Some natural oils dry by this mechanism, like linseed oil. They are sometimes called *siccative*. These oils consist of mixtures of triglycerides of non-saturated fatty acids, with double bonds that tend to become oxidized and turn into simple bonds, thus increasing the reactivity of the molecule. Although in the past formulations based upon non-modified vegetable oils were common, they have practically been banned from the market and replaced by synthetic or semi-synthetic resins.

The *cure* is a process that occurs by chemical reaction among some molecules of the mixture, but without participation of oxygen from air. It can occur at ambient temperature or at elevated temperature and it can be accelerated by heat, radiation and catalysts or by the combination of two or more of these methods. When two components are mixed shortly before application, the coating is called "two-component system". The cure can in some cases be accelerated by elevated temperatures (typically below 70 °C). The layers formed by chemical reaction are harder and chemically more resistant than those obtained by oxidative drying. These are by far the coatings with higher practical relevance. Examples of paints with cold curing are those using urea-formaldehyde resins, epoxy resins cured with amines, resins of non-saturated polyester and polyurethanes.

Finally, a *convertible coating* is one in which the binder is chemically different in the application form and in its final form.

17.3.1.2 Adhesion

When exposed to the effects of atmosphere or of the outer environment, a film with low adhesion will undergo degradation and either form blisters by absorption of water or vapour, or simply become detached from the surface and leave exposed areas. Loss of adhesion results in premature failure, and thus good adhesion between coating and substrate is crucial for the durability of a painted system.

Adhesion can be defined is a phenomenon that occurs when two surfaces become connected by interfacial molecular contact, in such a way that they become one unit. It refers to the capability of two surfaces, or objects, to cling together.

Adhesive forces develop when the coating is applied and also during the cure, and involve both physical effects and chemical reactions at the interface. The magnitude of these forces depends upon the nature of the binder and the surface and its nature can be covalent (primary valence) or secondary valence, such as hydrogen bonds or dipole forces. It is usually accepted that the forces that determine adhesion are:

- *Chemical bond near the interface* (roughly 100 nm to each side of the interface), of covalent or ionic type. These bonds at the interface are hard to detect due to the low thickness involved. It is however known that, under adequate conditions, some surfaces are able to form chemical bonds with the functional groups of the coating. This is the case of wood, of composites, of some plastics and of pre-coated surfaces. For example, coatings with functional groups such as hydroxyl or carboxyl adhere strongly to substrates containing similar groups;

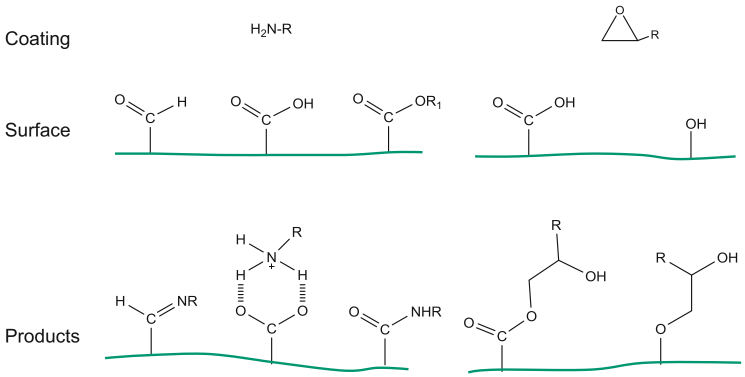

Fig. 17.2 Examples of chemical bonds between functional groups of the surface and the coating. Adapted from Ref. [8]

this is the case of finishing layers of acrylic-melamine over layers of polyester-melamine. Some of the possible reactions are listed in Fig. 17.2. Adhesion can also be improved by using adequate primers, such as organosilanes, used as primers to promote adhesion of resins to plastics reinforced with glass fibre. Organosilanes have been increasingly used on other substrates, such as minerals, metals and plastics, with the purpose of improving adhesion forces. In their application silanol groups are formed, which react either with the silanol groups of glass or with other groups (like metal oxides), forming chemical bonds.

- *Thermodynamic forces (W)*: These are reversible forces that tend to bring two materials together [4] and commonly described as

$$W_{ab} = \gamma_a + \gamma_b - \gamma_{ab}$$

In which
γ_a = surface energy of material *a*.
γ_a = surface energy of material *b*.
γ_{ab} = specific free energy at the interface.

These forces result not only from the formation of hydrogen bonds but also from electrostatic forces, such as the dipole–dipole attraction in molecules with permanent dipoles, between the part of the molecule with positive partial charge and the part with negative partial charge of another molecule, or the attraction among induced dipoles (London dispersion forces). Since all these forces are relevant only below 0.5 nm distance, the close contact between the substrate and the coating is essential [5] for them to act. These forces are approximately one order of magnitude lower than covalent bonds and so it is convenient to make them higher in order to reinforce adhesion. Since the adhesion force is proportional to the contact area, one way to increase adhesion is by extending the area of the surface to coat, which can be done by means of abrasive jets or by polishing the surface with grit before painting—Fig. 17.3. Further to the area

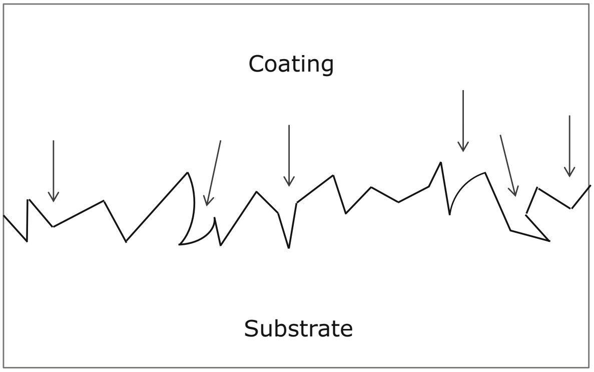

Fig. 17.3 Schematic representation of surface roughness on a microscopic scale

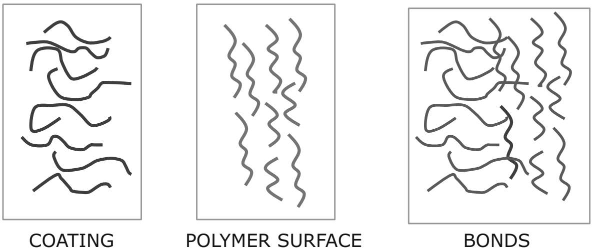

Fig. 17.4 Scheme of the diffusion of a paint in a polymer substrate

effect, it is essential that the paint penetrates the cracks and the recessed areas of the surface, for which its rheological properties, and namely its viscosity, are critical.

- *Diffusion*: This phenomenon can occur when two polymeric phases are put in contact; after the first stage of wetting, there is transport of segments of the macromolecules through the molecular network at the surface. This generates anchoring across a thickness of 1–100 nm—Fig. 17.4.

17.3.2 Volatile Components

Solvents are responsible for the dissolution of the resin and for the control of viscosity, thus allowing the application of the paint in the liquid state while promoting efficient wetting of the surface allowing the formation of a continuous layer.

Solvents are usually volatile substances and its evaporation is at the origin of the formation of the dry film—Fig. 17.5. Sometimes the expression *volatile vehicle* is used, in opposition to *fixed vehicle*. Although they evaporate after the application, volatile components play a major role in the paint. They determine the viscosity, the ease of application, the rate of evaporation and also the adhesion and the occurrence of internal mechanical stresses in the dry film.

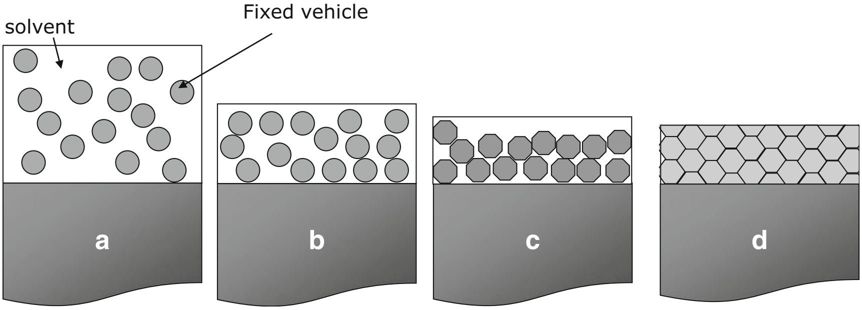

Fig. 17.5 Mechanism of formation of a dry film starting from an emulsion:. (**a**) liquid emulsion; (**b**) after partial evaporation; (**c**) deformation to a polyedric structure ; (**d**) dry film

Volatile components can be classified as:

- *True* s*olvents*: these are substances that effectively dissolve a certain resin, with total miscibility for any proportions.
- *Auxiliary solvents*: these are substances that cannot dissolve the resin by themselves but which allow dissolution when added to the true solvent.
- *Diluents*: these are organic compounds that have no dissolving power but which are compatible with the solvents; their main role is to help control the properties of the liquid mixture and control the curing rate, while increasing the volume at low price.
- *Thinners*: these are liquids added to the formulation with the aim of decreasing the viscosity.

Finally, *filmogenic solvents* are those that, further to the dissolution of the resin, have the ability to become incorporated in the dry film by polymerization, like styrene. Sometimes, commercialized products like diluents are formulated with several components. For example, in the case of cellulosic diluent, esters or ketones are used together as solvents, plus diluents (aromatic hydrocarbons) and alcohols (auxiliary solvents). That is, a good diluent is in practice made with several substances.

Traditionally, paint industries used a large variety of solvents, such as aliphatic hydrocarbons (white spirit), aromatic hydrocarbons, alcohols, esters, acetones and glycols. In the past three decades, the environmental concerns and the legislation have imposed tight limits to the use of volatile organic compounds (VOC), which has led to drastic changes, towards water-based formulations. Compared to organic solvents, water has the advantage of being totally clean from an environmental perspective, and in addition it has low cost. Its main drawback is the high melting point, compared to the organic solvents, which causes risk of freezing in cold climates. Further, water does not dissolve by itself most resins, and so it has to be used together with a real solvent; that is, water usually works as a diluent.

17.3.3 Pigments

Pigments are solid particles of dimensions typically below 1 μm, which are insoluble in the binder and which constitute a finely divided phase dispersed in the continuous phase, i.e. a colloidal dispersion. Pigments are usually arranged in agglomerates and they confer several properties to the coating, namely colour, opacity, impermeability and corrosion protection.

Pigments can be classified into three groups:

- *Coloured*: they give both colour and opacity to the paint. Some dyes are soluble in the binder, and so they provide colour but not opacity (covering power), which means that they are not pigments.
- *Charges or extender pigments*: these are particles that are insoluble in the binder but that give neither colour nor opacity to the paint. They affect the consistency of the paint and increase its final thickness, while lowering the final cost and improving the mechanical properties of the dry film, particularly abrasion resistance. Examples of charges are talc $Mg_3Si_4O_{10}(OH)_2$, quartz (SiO_2) and alumina (α-Al_2O_3).
- *Anti-corrosion*: these are pigments that act chemically or electrochemically, by inhibiting the dissolution of the metallic substrates on which the paint is applied.

The most relevant properties of the pigments used in paints are described below.

17.3.3.1 Optical Properties

The main optical properties of pigments are colour and opacity. The mechanisms capable of conferring colour to an object are various, namely refraction, reflection, light dispersion, diffraction and radiation absorption [6]. In pigments, the colour results mainly from absorption and reflection processes. Thus, a blue pigment is that which reflects the blue radiation and absorbs all the other parts of the visible spectrum. A white pigment reflects all the wavelengths of the incident radiation, whereas a black pigment absorbs generically all the radiation.

Opacity is correlated with refraction. When a beam of light goes from one material to another, it undergoes *refraction* at the interface between the two materials, i.e. the direction of the light beam is altered. Refractance depends on the wavelength of the radiation and on the optical density of the two materials. For each medium, the optical density is measured by its *refractive index*, n; a dimensionless parameter defined as the ratio between the speed of light in vacuum, c; and the speed of light in the material, v:

$$n = \frac{c}{v}$$

The refractive index varies with the wavelength, which causes dispersion of light, i.e. the splitting of white light as happens with prisms and with the rainbow. For

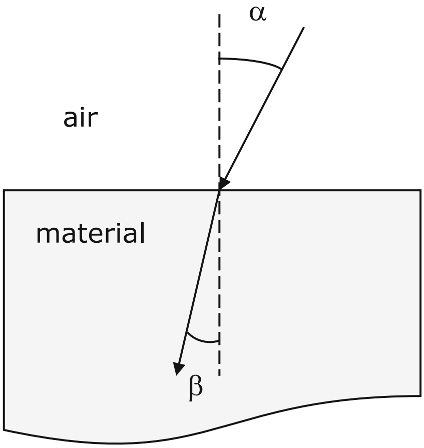

Fig. 17.6 Refraction of light

visible light most transparent media have refractive indices between 1 and 2, which means that the speed of light is one to two times slower than in vacuum.

When light moves from one medium to another, it changes direction, i.e. it is *refracted*, i.e., it is bent—Fig. 17.6. If it goes from a medium with refractive index n_1 to one with refractive index n_2, with an incidence angle to the surface normal of θ_1, the transmission angle θ_2 can be calculated from Snell's law:

$$n_1 \sin \theta_1 = n_2 \sin \theta_2$$

If there is no angle θ_2 fulfilling Snell's law, i.e. if

$$\frac{n_1}{n_{2_1}} \sin \theta_1 > 1$$

then the light cannot be transmitted and will instead undergo total reflection.

In a paint film we have the pigment in contact not with air, but with the binder. As a consequence, the higher the difference between the refractive indices of the pigment and the binder, the more opaque the film will be.

17.3.3.2 Shape of the Particles

The shape of the particles, as well as their dimensions and distribution, will influence the flow properties, the gloss, the ease of dispersion and resistance of the paint to weathering. As far as shape is concerned, particles can be classified as primary particles or as particle aggregates. Particle aggregates generally have more complex shapes and larger dimensions, and consequently tend to reduce the brightness of the final coating.

17.3.3.3 Dispersibility and Pigment Concentration

The properties of the paint are greatly dependent upon the physics and chemistry of the pigment/vehicle interface. One important feature is the area of the interface, which is usually extremely large. Let us take a particle with a diameter of 1 mm, and divide this particle successively into smaller particles of even size; if we calculate the total surface area at any stage of subdivision, we get a good idea of how fast the interfacial area increases as the particle size decreases—Table 17.1.

Depending on the size and geometry of the pigments and on the properties of the binder, different degrees of dispersion can be achieved. Ideal dispersion corresponds to a limit situation with each pigment particle separated and totally surrounded by the binder. In colloidal systems, dispersion is reached when the potential at the surface of the particles exceeds a critical value, called the zeta potential [7]. The zeta potential is related to the stability of colloidal dispersions and is known by the zeta Greek letter, i.e. ζ-potential. More specifically, its value indicates the degree of repulsion between adjacent, similarly charged particles in a dispersion. For small molecules and particles, a high zeta potential will confer stability, i.e. repulsion will predominate and thus the solution or dispersion will resist aggregation. When the potential is low, attraction exceeds repulsion and so the dispersion will break and flocculate. Therefore, colloids with high zeta potential (negative or positive) are electrically stable, whereas colloids with low zeta potential tend to flocculate [8]. Table 17.2 gives the ranges of ζ-potential and the corresponding behaviour. For water-based coatings the zeta potential is approximately 30 mV and so pigments of very small dimensions, namely nano-sized particles have a great tendency to flocculate, making dispersion hard to deal with.

In a simple way, decorative paints can be described as a mixture of pigment, binder and solvent, in variable proportions. Naturally, after drying the composition becomes dominated by the pigment/binder ratio, although often there is also some air trapped in the film. One of the most important parameters in the description of a paint is the *pigment volume concentration* (PVC), which consists of the volume fraction of the pigment (generally expressed in percentage) in the total volume of the dry film:

$$\mathrm{PVC} = \frac{V_\mathrm{P}}{V_\mathrm{P} + V_\mathrm{L}} \times 100\%$$

in which V_P = volume of pigment and V_L = volume of binder. If we imagine the limit situation of only pigment and no binder, then PVC = 100 %. As we add increasing amounts of binder, in a first stage we will have numerous empty spaces, where air is entrapped among the pigment particles. The air will be gradually replaced by binder as the content of binder increases, until all the particles become

Table 17.1 Influence of particle size on the surface area

Diameter of particles	Number of particles	Total area of particles
1 mm	1	3.14 mm^2
0.1 mm	10^3	31.4 mm^2
0.001 mm = 1 μm	10^9	31.4 cm^2
0.1 μm	10^{12}	314 cm^2
0.001 μm = 1 nm	10^{18}	3.14 m^2

Table 17.2 Zeta potential vs. stability of dispersions

ζ-potential (mV)	Dispersion stability
0 to ±5	Rapid coagulation or flocculation
±10 to ±30	Incipient instability
±30 to ±40	Moderate stability
±40 to ±60	Good stability
Higher than ±61	Excellent stability

totally surrounded by the binder (total wetness). To this concentration of pigment, we call the *critical pigment volume concentration* (CPVC). From then on, the particles become increasingly separated, i.e. better dispersed in the vehicle [9].

These two parameters, PVC and CPVC, are crucial in the final properties of an organic coating. Above the critical concentration, the amount of binder is insufficient to fill the gaps between pigment particles and therefore the film becomes porous. In coatings with good formulations and adequate dispersion, particles do not touch one another. In a porous coating, with high pigment concentration, porosity is deleterious for corrosion protection of the underlying metal substrate. Thus, paints with high pigment content are generally not effective for corrosion protection. On the other hand, low pigment concentration results in lower covering power and in higher permeability, and thus to easy formation of blisters—Fig. 17.7.

Gloss and covering power are also functions of the pigment content. A glossy paint usually has PVC of 20 % or lower, whereas a reasonable covering power requires a PVC of at least 5 %.

17.3.3.4 Classes of Pigments

Pigments can be organic or inorganic. Inorganic pigments are usually metal oxides and they are the most common [2,9].

- Titanium dioxide (TiO_2): it is the most used pigment for white coatings or for light colours. It provides opacity and chemical resistance.
- Aluminium: it has very high covering power and provides metallic brightness. In addition, it gives good resistance to the penetration of moisture from the air, which makes it effective for corrosion protection.
- Iron oxide: it is widely used in the paint industry. Some are produced industrially (synthetic), although most are mineral. The most relevant forms are:

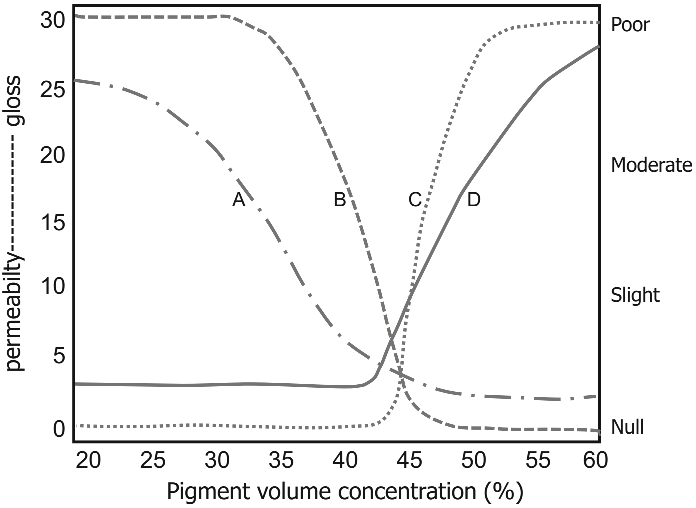

Fig. 17.7 Effects of the PVC on the protection provided by an organic coating

Red iron oxide (Fe_2O_3): it is commonly used in the formulation of anti-corrosion primers. It has a typical reddish colour.

Black (Fe_3O_4) and yellow ($Fe_2O_3 \cdot H_2O$) iron oxides: they are widely used in paint formulation. They provide opacity and colour.

Micaceous iron oxide: similarly to the red iron oxide, it has the chemical formula Fe_2O_3. It differs from the red oxide in the lamellar shape of the particles (like mica) and in the lead-grey colour. It is used in anti-corrosion paints.

- Other common pigments are those based upon chromium, zinc and cadmium oxides.
- Organic pigments: these are of organic nature, i.e. based upon carbon chains, although they can also include metal atoms in their structure. The properties of organic pigments are quite different from those of inorganic ones: particle dimensions are significantly smaller, which decreases the effects of light dispersion and thus reduces opacity. On the other hand, they tend to tend to have lower resistance to organic solvents.

17.3.4 Additives

Additives are substances that are added to the formulation in low concentrations, with the aim of conferring specific properties either to the liquid paint or to the dry film.

Additives are commonly classified according to their aim. So, we have [2,9]:

- Driers: these reduce the drying time, by a catalytic effect in the film formation.
- Dispersing/stabilizers: they improve dispersion and reduce the tendency to sedimentation of pigments during storage.
- Anti-skin: they prevent the formation of a dry layer on the surface of the liquid paint (skin) during storage.
- Plasticizers: they improve the flexibility of the dry film.
- Levellers: they give the dry film a good levelling, thus preventing the marks left by the paintbrush.
- Anti-foam: they prevent the formation of foam during the application of the paint.
- Thixotropic agents: they prevent the dripping from the brush or on vertical surfaces; usually they consist of organosilicates or amides with low molecular weight.
- Antifouling: they protect the paint from the attack of fungi, algae and bacteria, either during storage or after application. Some of these additives have been under environmental pressure due to their toxicity.

17.3.5 Classification of Paints

Paints can be classified in different ways, depending on the properties considered. The most common classifications are based upon the chemical nature of the solvent or upon the cure process. Depending on the chemical nature of the solvent, paints can be called aqueous based, solvent based (as the binder is dispersed in an aqueous phase or dissolved in an organic solvent) or paints without solvent. Concerning the cure, they can have physical drying, i.e. when the film is formed by evaporation of the solvent (case of the aqueous dispersions), or by chemical reaction, in which the first step of physical drying is followed by a chemical reaction.

17.4 Paint Degradation

Every organic material is susceptible to destruction caused by atmospheric agents, which consist of ultraviolet radiation, temperature, moisture, oxygen and pollutants [8]. Let us look briefly at each of these agents, as well as of its effects.

17.4.1 Aggressive Agents

17.4.1.1 Ultraviolet Radiation

Ultraviolet (UV) radiation is the main source of energy for paint degradation. Radiation reaches surfaces either directly (solar radiation coming through the atmosphere) or through diffuse radiation (indirect), which results from dispersion of radiation by particles like water droplets, dust or even by the gas molecules of air.

Solar radiation has a spectrum that goes from 200 to 3,000 nm wavelength. Of these, only a small part reaches the surface of our planet. Thus, the oxygen layer, located at about 75 km altitude, filters the radiation with wavelength below 175 nm. This is the radiation with highest energy, since the energy is inversely proportional to the wavelength. The ozone layer, at 20–30 km altitude, filters the UV radiation in the range of 175–290 nm and, finally, the clouds filter the infrared radiation above 1,400 nm, so that the wavelength window that reaches the surface of Earth is approximately 300–1,400 nm.

This radiation corresponds to the following distribution:

Radiation	Wavelength (nm)	% total radiation
UV-B	285–315	0.4 %
UV-A	315–400	5.6 %
Visible	400–780	50.0 %
Infrared	780–1,400	44.0 %

This distribution is also seen in Fig. 17.8. The amount of diffuse radiation is larger in the UV range than in the other energy ranges. This means that the effects of diffuse UV radiation are felt even on cloudy days. This is the radiation that has a higher effect on paint degradation. Most resins undergo degradation in the range 280–320 nm, i.e. in the UV range. Note that the most destructive radiation, UV-B, corresponds only to a very small fraction of the spectrum, and thus its effect is comparatively unimportant [10].

UV radiation possesses enough energy to break molecular bonds in polymers, thus transforming the macromolecules in progressively smaller chains, until they turn into molecules with low molecular weight, which can become soluble or just leached by rainwater. In this way, the paint film loses thickness; further, it becomes harder and brittle, as a result of the degradation of the relatively elastic macromolecules. The degree of ageing of the film can be assessed by the loss of the dry film thickness (DFT) and results from the evolution of the process from the surface, towards the underlying substrate. For the polymers commonly used in paint formulation, the rate of thickness reduction is typically in the range 5–25 μm/year. It is possible to get better performances with families of polymers with better resistance to UV radiation, like the polymethyl methacrylates, the fluorinated polymers (e.g. poly-vinyl fluoride), silicon-modified polyesters and aqueous-based poly-vinyl polymers with molecular weight above 10^6.

The effect of radiation can also be controlled by using UV absorbers as additives; these are substances that absorb UV radiation, transforming it into thermal energy and thus controlling the breaking of polymer chains. There are several additives available in the market with this property, which act on wavelengths 280–350 nm; this is the case of benzotriazole and of benzophenone derivatives.

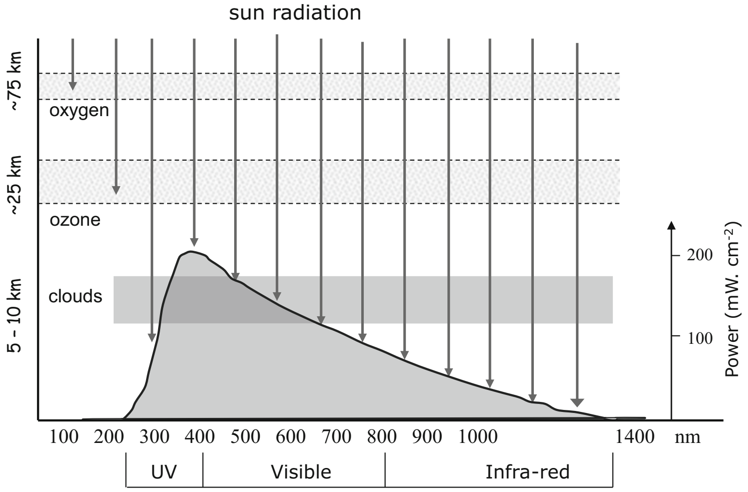

Fig. 17.8 Distribution of energy for the sun irradiation spectrum (adapted from Schmid 1988, Ref. [10])

17.4.1.2 Temperature

While the UV radiation causes polymer degradation by breaking chemical bonds, infrared radiation has a thermal effect that results in heating of surfaces. The degree of heating depends on the coefficient of thermal absorption, which is a function of the colour, and thus it depends on the pigment. The temperature of an irradiated surface can reach tens of degrees Celsius above ambient temperature, depending also on the degree of thermal insulation, i.e. of the thermal conductivity of the surface. Materials such as wood, plastics and surfaces insulated from the rest of the structure (metal façades, car roofs) will reach higher temperatures as they cannot dissipate heat by conduction to the colder parts of the structure. Figure 17.9 shows an estimation of the increase of temperature for different colours of the coating.

17.4.1.3 Humidity and Condensation

Air always contains a certain amount of water in the form of vapour. We know from physics that a certain volume of air has a limited capacity for containing water vapour, above which water condenses, according to the plot in Fig. 17.10. As an example, let us consider 1 m^3 of air, containing 10 g of water. At 14 °C the air is sub-saturated, i.e., it is below saturation. The relative humidity (RH) is a measurement of the degree of saturation, and in this case its value is roughly 80 %. At 25 °C the air can take even more water, i.e. although it contains the same amount of water, the air will become drier. However, if during the night the temperature drops to, for example, 5 °C, then the water content that corresponds to saturation will be only 6.8 g, and therefore the excess, of 3.2 g, will condensate as liquid water, in the form of drew drops [10].

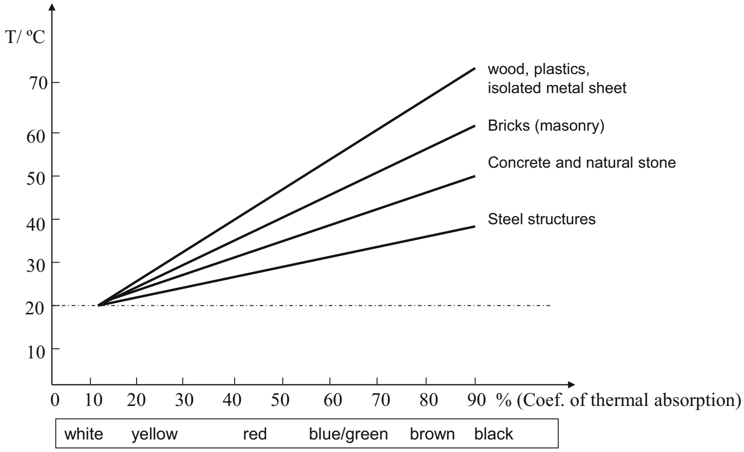

Fig. 17.9 Heat accumulation and colours of organic coatings. Adapted from Ref. [10]

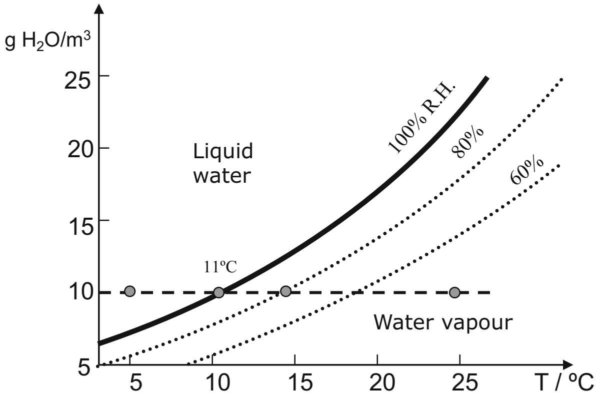

Fig. 17.10 Relative humidity (R.H.) and condensation (adapted from Ref. [10])

Liquid water is a degradation agent of organic coatings and often of the substrates at gaps in the coating. Water can act in various ways, from the dissolution of pollutants from the atmosphere (making their effect stronger) to the loss of adhesion to the surface and even to the corrosion of substrates, when they are metals. Often the effect of dew is worse than that of rain, as the dissolution of acid pollutants in small volumes of water can lead to high concentrations and thus to increased aggressiveness. The degree of condensation is a function of various parameters, such as the orientation (horizontal surfaces have more dew), the colour (dark colours keep dew for a longer time) and the degree of night cooling (clear nights, with no clouds, are more favourable to condensation).

17.4.1.4 Acid Pollutants from the Atmosphere

The most important pollutants are sulphur dioxide (SO_2), nitrogen oxides (NO_x) and chlorides (Cl^-). SO_2 results from the burning of fuels and of coal, either in energy production plants or in industrialized areas, generally speaking.

SO_2 reacts with the moisture from air, forming sulphurous acid which later becomes converted to sulphuric acid by reacting with oxygen from the air. Winds can easily transport these acids to different geographical regions, leading to acid rain in areas that can be a long way from their origin.

Nitrogen oxides are produced in combustion processes (including cars) and undergo a similar process, producing nitrated acids, such as nitric acid. Of these two, sulphuric acid has a stronger degradation effect; unlike nitrated acid, sulphuric acid does not evaporate under the heat from solar radiation. On the contrary, solar radiation causes water evaporation and thus a decrease in the size of the droplets, which consequently become saturated and thus more aggressive.

Chlorides are present mainly in the form of sodium chloride from the sea. Chlorides are very aggressive to metal substrates and cause corrosion when combined with high humidity, even across the paint protective coating.

17.4.2 Symptoms and Mechanisms of Degradation

17.4.2.1 Loss of Gloss

Gloss is related to the reflection of an incident visible light beam, indexed to a certain angle of incidence, normally 20° or 60°. The reduction of gloss, which

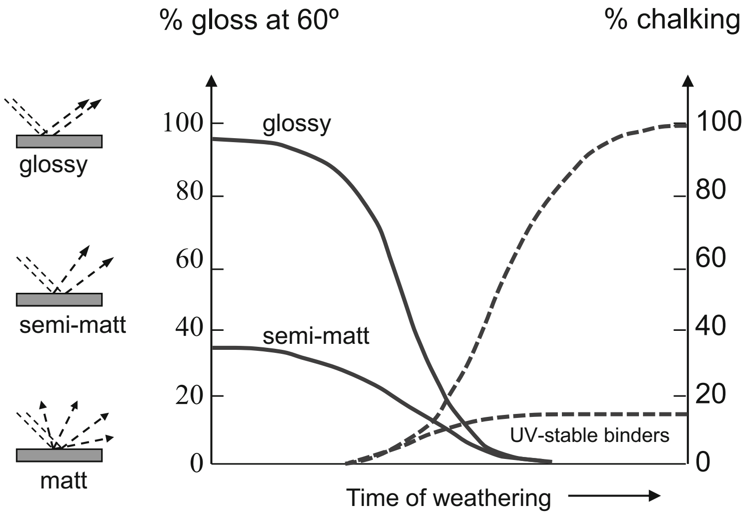

Fig. 17.11 Reduction of gloss and beginning of chalking for coatings with different finishings. Adapted from Ref. [10]

results in a matte surface, is usually the first symptom of degradation of an organic coating, and precedes the stage of real loss of thickness of the paint—Fig. 17.11.

17.4.2.2 Chalking

Chalking is a process of ageing that consists of the detachment of particles from the surface of the film, making the paint powdery, resembling chalk. This powder is whitish and it is usually possible to find the original colour of the surface by removing the outer layer with the hands or rubbing with a cloth. This phenomenon is a consequence of several factors, namely UV radiation and heat but also moisture and oxygen. In tropical regions, with high humidity and a large number of sunlight hours, chalking is more intense than in cold climates or dry mountain regions. This is because moisture causes swelling of the paint, making it less dense and thus more permeable to UV radiation. The energy transmitted by the radiation, together with the oxygen from the air, causes chemical reactions of breaking, fission or cracking of the polymer molecules; the result is a loss of the binder and thus an increase of the pigment concentration. The cohesive forces thus decrease and the inorganic particles (pigments and charges) become loose from the matrix.

Chalking usually starts when the loss of gloss is still in progression—Fig. 17.12—and can be controlled using UV absorbers.

17.4.2.3 Cracking and Loss of Adhesion

The last stage of the degradation process is the detachment of particles of paint, in the form of small flakes. This cracking of the finishing layer is caused by the different elastic properties of the two layers. The outer layer, in its process of ageing by weathering and as a result of the breaking of macromolecules becomes less elastic, as described above. This effect, however, is superficial, and thus the underlying polymer remains elastic; the two layers thus respond differently to the action of the environment (temperature variations and cycles of wetting/drying), which causes cracking of the less elastic layer—Fig. 17.13.

This process is in some way comparable to the method used for cracked finishings (known as *craquelé*), which consists of applying a very elastic layer,

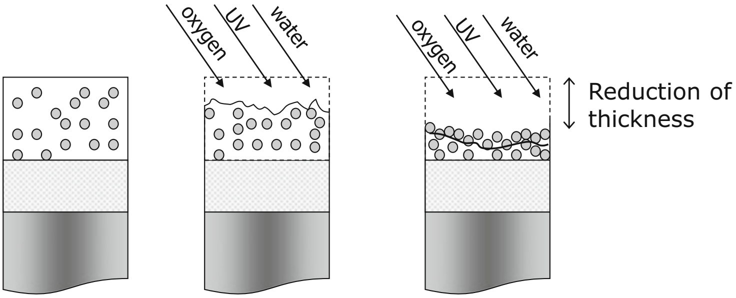

Fig. 17.12 Mechanism of chalking

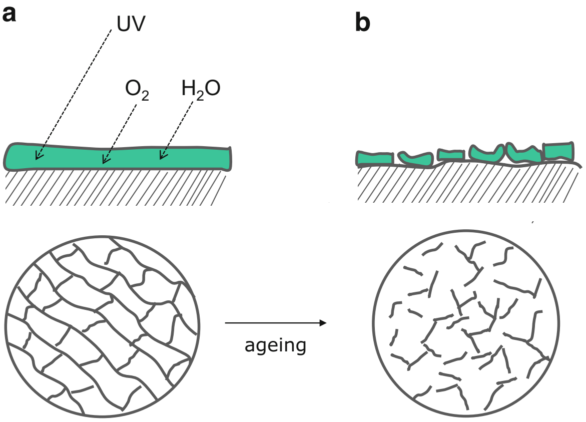

Fig. 17.13 Cracking caused by UV radiation (adapted from Ref. [10])

followed by a varnish with low elasticity and with fast drying. As it dries, the lacquer becomes cracked and produces a "cracked" look. In the case of paints this process occurs naturally, although in some cases the flakes can remain attached to the surface for a relatively long time.

17.5 Selection of a Paint System

Paints are the class of coatings more used all over the world, in a wide range of areas and with many purposes. Nevertheless, the problems associated with each kind of surface are very specific, either due to the physical–chemical nature of the surface, or due to the desired function of the coating, or even due to the action of the environment to which the coating will be exposed. We will now go briefly into the most common applications of paints.

17.5.1 Masonry

Mineral surfaces such as cement walls, have specific properties that are crucial on the durability of the paint layer, and which are:

- The porosity of the substrate
- Water absorption permeability to water vapour
- The alkaline character
- The presence of water-soluble salts

Porosity can be defined as the volume fraction of the material that is filled with air, i.e. that corresponds to empty spaces. Naturally, a highly porous material is capable of absorbing large amounts of water, with significant consequences on the thermal conductivity of walls. Evaporation of the water from the walls is a process that absorbs much energy and thus it causes fast cooling, with severe consequences on the comfort and on the domestic energy consumptions for heating. On a different line of reasoning, penetration of water, oxygen and other aggressive agents from the outside can cause corrosion of the steel reinforcement, with degradation of the structure and repair costs. Thus, it is advantageous to use outer coatings that are hydrophobic, in order to prevent water absorption, while keeping some permeability to the water vapour coming from the inside.

The alkaline character of construction materials is also crucial in the choice of the paint properties. Cement is rich in calcium hydroxide, which causes a pH of approximately 12 to the solution filling the pores of concrete. Coatings must therefore be resistant to alkalis and also be free of oils susceptible to saponification.

Finally, the influence of atmospheric contaminants and the presence of salts in construction materials cause a high content of soluble salts, which requires the use of paints with high permeability to water vapour, in order to prevent the formation of blisters due to osmosis phenomena.

The paint systems most commonly used for masonry are water-based polymeric emulsions (latex paints), solvent-based polymer coatings, water-based silicates and impregnation and consolidation agents.

17.5.2 Wood

Wood has high porosity, nearly 50 % of the total volume. This porosity differs from that of concrete because it comes in the form of oriented pores, with 10–15 mm diameter, which follow the direction of the cellulose fibres. This results in a hygroscopic material, which absorbs and releases large amounts of water, as the atmospheric humidity varies. High water absorption leads to variation of the total volume, sometimes up to 2–3 %, which is a property of wood. Under high humidity, wood can reach water contents up to 20%, at which moss and lichens develop. In order to prevent and control this phenomenon, fungicides are usually added to the formulation, like zinc oxide and barium metaborate. These additives are generally added to the top layer, thus preventing characteristic the growth of mould on the surface.

The effects of radiation on wood are felt on the outer layers, by a mechanism similar to polymers in general. This effect, which is stronger in the presence of moisture and oxygen, is visible by a typical greyish colour and by an eroded surface, with low capability of providing adhesion to organic coatings.

An important factor to an organic coating for wood is elasticity. Elasticity, however, is lost with time, as a result of the formation of cross-linking between polymeric chains. It is thus better to use binders with good elastic properties, as they are less prone to the formation of cross-links; this is the case of emulsions of acrylic or vinyl emulsions. These coatings, however, have a drawback, which is the tendency to stick together when put in contact. This can be a great nuisance, for example, when a window or door is closed leaving the two painted surfaces in close contact, since the window or door may become blocked. Another problem is the tendency to retain dirt, particularly when the painted surface becomes hot due to sun radiation.

Concerning water and moisture, although it is important to prevent water penetration, it is also desirable to keep some permeability to water vapour, in order to allow drying of the wood across the coating. For protection of wood, lacquers are sometimes chosen, for aesthetical reasons. However, it should be considered that transparent coatings are not only more permeable to UV radiation but they are also more prone to ageing due to radiation. Thus, as a general rule, the durability of lacquers (varnishes) is lower than that of other pigmented organic coatings.

17.5.2.1 Pretreatments and the Role of Primers

In a paint system for wood, the primer has several functions:

- It impregnates the outer layers of wood, reinforcing the bond between the wood and the top layer. This can only be achieved with a low viscosity primer, capable of penetrating the small grooves of the surface.
- It limits the absorption of water by the wood cells.
- It stops the growth of moss and fungi; this is achieved by the use of fungicides (e.g. of lead or of barium) in the formulation.

Freshly cut wood, which still has the cells partly open, allows better integration by the primer. Aged wood, in contrast, has the outer cell layers more destroyed and so the adhesion of the coating is not good unless a layer of 2–3 mm, i.e. the grey layer, is removed.

In the past twenty years, a major change in the formulations has taken place, from the classical primers, solvent-based, to water-based emulsions, acrylic or alkyd, due to environmental concerns.

17.5.2.2 Semi-transparent Paints

The natural beauty of wood frequently causes architects and designers to choose non-pigmented varnishes to apply on wood. These varnishes have good durability in dry atmospheres but they are not very protective in most climates. Not only do they allow the access of UV radiation to the wood surface, but they also suffer degradation themselves due to the reaction of the polymer, which results in water penetration and further degradation of the wood. In most paints these effects are delayed by the addition of pigments that are UV absorbers, but these pigments are coloured, and so their acceptance in the market is not easy. Recent years have seen the development of semi-transparent varnishes, which have 2–3 % of pigments, typically synthetic iron oxides, red, brown or yellow; these pigments absorb UV radiation while they keep partial transparency, this allowing visualization of the natural pattern of wooden surfaces.

17.5.3 Iron and Ferrous Substrates

On iron or steel, the primer has not just the function of promoting adhesion between the top coat and the substrate; it also has an anti-corrosion function. Corrosion is electrochemical in nature and it only occurs in the presence of oxygen and water. One of the consequences of corrosion is the formation of blisters in the organic coating, due to the accumulation of corrosion products at the metal/coating interface, which generates osmotic pressure [11].

The organic coating has a barrier effect, by which it hinders the penetration of aggressive agents down to the metal. However, protective as it may be, the coating has always some permeability to aggressive agents such as water, oxygen and ions, namely chloride ions. Corrosion inhibitors (substances that decrease the rate of the corrosive process) soluble in water can be added in the primer formulation. When water reaches the primer, these soluble pigments become dissolved and are leached towards the metal surface, where they will hinder the corrosion process. Adhesion between the paint and the metal is extremely important and for that an adequate preparation of the surface needs to be made, including etching (by abrasion, flame or acid cleaning) and normally a passivation pretreatment; these pretreatments were made traditionally using chromic acid until these were banned for public health reasons and actually phosphoric acid and other pretreatments are used.

17.5.4 Zinc and Galvanized Steel

Galvanized steel is commonly used for many applications, namely in car bodies. Coil-coated steel, with zinc coatings of 7–10 μm, is normally used. Zinc provides cathodic protection to steel, i.e. when the two are in contact, they make a galvanic couple, in which zinc is corroded preferentially and steel is the cathode. This means that even if steel gets exposed, it will be protected from corrosion. As far as the coating is concerned, polymer ageing and formation of blisters happen just like in ferrous substrates.

In the cathodic protection there is formation of an alkaline environment that may attack the resin by a saponification reaction, causing loss of adhesion to the substrate. Passivation treatments can also be applied, with the aim of decreasing the metal activity and thus improve corrosion resistance of the substrate. Industrially, paint systems with two or three layers are applied, and a final thickness above 100 μm is recommended.

17.5.5 Aluminium and Light Alloys

Aluminium and its alloys resist well to corrosion in moderately aggressive media, thanks to the spontaneous formation of a film of protective oxides, in a phenomenon called "passivation".

In the presence of aggressive ions, such as chlorides, the passivation layer can be destroyed locally, and then corrosion develops, producing pits on the surface. Corrosion protection can be achieved in one of two ways: either by anodizing, which consists of the growth of a thick aluminium oxide film, with reinforced protection, or by applying an organic coating. This last method is very much used in structures, for example, in windows. One of the common causes for bad adhesion is inadequate treatment of the metal surface, namely cleaning. For many years, the durability of painted systems was extended by using chemical conversion treatments, by chromatation or etching plus chromate-pigmented primer. In the past decade, the use of chromates has been banned in most of the world and for most applications, due to the toxicity of Cr(VI) compounds. Alternative pretreatments have been developed, generally based upon silicates, phosphates and other compounds of low toxicity. Some studies have also shown that primers rich in magnesium or in magnesium alloys can also be protective to aluminium, in the same way as zinc protects steel.

17.6 Recent Trends

The growing search for environmentally friendly materials, with longer lifetime and competitive costs, has led to important developments, aimed at improving specific properties. Some examples are described below.

17.6.1 Silicate Coatings

Silicate coatings have been growingly used on mineral substrates, due to a number of attractive properties, such as resistance to moisture, low permeability to water, high permeability to water vapour and resistance to microorganisms [12]. These are hybrid coatings, consisting of an inorganic binder (usually potassium silicate) plus an organic binder (acrylic or styrene-acrylic dispersion) that corresponds only to about 5 % of the formulation. The inorganic binder chemically reacts with the substrate, in a reaction called *petrification*. The bond is chemical and therefore it repels liquid water, while it remains permeable to water vapour, thus making the coating less prone to blistering. The major limitations are the lower resistance to chalking and the need for a substrate capable of reacting with the silicate, thus excluding organic substrates and repainting.

17.6.2 Paints Based on Nanocomposites

The term nanoparticle refers in principle to particles with dimensions below 200 nm. Nanoparticles have unique properties that result from their small dimensions. An important property is transparency, which is caused by the fact that their size is below the wavelength of visible light and thus they do not disperse light. Another characteristic is that surface properties are enhanced when compared to larger particles, for which the area per unit mass is much smaller. Aqueous dispersions of nanocomposites can be produced by polymerization of an emulsion in which an organic polymer conjugates with silica inorganic particles of 10–20 nm, thus making the homogeneous incorporation of nanoparticles in the binder a key factor in the final properties of the coating. The films obtained in this way depict transparency and hardness, combined with good elasticity, heat resistance and low flammability.

17.6.3 Self-Cleaning and Photocatalytic Organic Coatings

The hygienic effect is important in external façades but also in indoor walls, particularly in public buildings like schools or hospitals. Research has been made on paints with photocatalytic effect for the oxidation of organic matter. Titanium dioxide (TiO_2), in the form of anatase, has this capability. Under the effect of UV radiation, anatase becomes excited and, in contact with water and oxygen, hydroxyl radicals ($OH\cdot$) are produced, which will decompose the organic matter on the surface of the coating, resulting in water and CO_2, which is released to the atmosphere.

Beyond this effect, anatase has another photocatalytic action, which is to promote the decomposition of nitrogen oxides (NO or NO_x), thus acting as an atmosphere decontaminant. These pollutants are particularly dangerous in urban and industrial areas and they have as side effects acid rain and photochemical fog, both dangerous for humans and for the environment. TiO_2 absorbs UV radiation, generating hydroxyl radicals that react with NO or NO_2, forming nitric acid, which is then washed by rainwater. This kind of approach has been tested on coatings for buildings.

References

1. Munger CG (1984) Corrosion prevention by protective coatings. NACE—National Association of Corrosion Engineers, Houston, TX
2. Nylén P, Sunderland E (1965) Modern surface coatings. Interscience, London
3. Gaynes NI (1967) Formulation of organic coatings. D. Van Nostrand Company, Inc., New Jersey
4. van Eijnsbergen JFH (1994) Duplex Systems: Hot-dip Galvanizing plus Painting, Elsevier Science B.V., Amsterdam, The Netherlands

5. Oil and Colour Chemists' Association (1993) Surface coatings, vol 1 raw materials and their usage. Chapman & Hall, New York.
6. Tilley R (2000) Colour and the optical properties of materials. Wiley, Chichester
7. Barnes GT, Gentle IR (2005) Interfacial science: an introduction. Oxford University, New York
8. Greenwood R, Kendall K (1999) J Eur Ceram Soc 19(4):479–488
9. Wicks W, Jones S, Pappas P (1999) Organic coatings- science and technology, 2nd edn. Wiley, New York
10. Schmid EV (1988) Exterior durability of organic coatings. FMJ International Publications Limited, Redhill, Surrey
11. Grundmeier G, Simões A (2003) Corrosion protecting by organic coatings. In: Stratmann M, Frankel GS (eds) Encyclopedia of electrochemistry, vol 4. Wiley, Weinheim
12. Schwartz M, Baumstark R (2001) Waterbased acrylates for decorative coatings. European Coatings Literature, Vincentz, Hannover

Environmental Impact and Life Cycle Evaluation of Materials

18

Fernanda Margarido

Abstract

This chapter begins with the presentation of the factors responsible for the sustainability of the construction industry, as it should try optimising its production cycle whilst taking into account materials such as energy and keeping them within thermodynamic limits. Furthermore, the treatment of C&DW is discussed, considering that waste produced should always be reused and/or recycled whenever possible and that which cannot be reused should be sent to landfill, without posing threat to the environment. Another important aspect herein considered is that the construction industry has a positive impact as a large recycling industry of waste and by-products produced in other areas of industry, transforming them and using them in the production of alternative construction materials. Subsequently, detailed information is afforded concerning the interest in the life cycle analysis of this sector increased with the publication of legislation on environmental control, including integrated pollution control and better production techniques.

Keywords

Construction industry • Construction and demolition wastes (C&DW) • Environmental impact • Sustainability • LCA • Recovery of C&DW • Characterisation • Recycled materials • Ecotoxicological effects

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M.C. Gonçalves, F. Margarido (eds.), *Materials for Construction and Civil Engineering*, DOI 10.1007/978-3-319-08236-3_18

Abbreviations

APA	Portuguese Environment Agency
CFC	Chlorofluorocarbons
C&DW	Construction and demolition waste
ELW	European List of Waste
EPA	Environmental Protection Agency (USA)
EU	European Union
GDP	Gross domestic product
LCA	Life cycle analysis
LNEC	Portuguese National Laboratory of Civil Engineering
MS	Member States of the European Union
MSW	Municipal solid waste
OWM	Organised waste market
SILOGR	Portuguese Information System for Waste Management

18.1 Introduction

The construction industry is one of the main and oldest activities that has aided the economic and social development of nations, thanks to its big impact on the economy, generating capital and creating many jobs.

This sector is not an environmentally friendly one by nature. It uses space that previously belonged to nature and is responsible for consuming large quantities of our planet's natural and energy resources, used to produce the wide range of materials that it incorporates, having a considerable impact on the environment.

It creates pollution through CO_2 emissions and is the third biggest source of emissions in the industrial sector not only on a global level but also within the European Union (EU) [1]. It is responsible for producing waste that contaminates the soil, visual pollution as well as waterline pollution, blocking city drains, which clog or silt up water courses, making them susceptible to flooding; it spreads disease-transmitting agents and also attracts other types of waste, etc. Some of these problems, despite being easy to detect because they can lead to the degradation of urban areas and the quality of life of communities, are very difficult to quantify.

However, construction work can, from an environmental and economic perspective, have a positive impact as a large recycling industry, not only with waste produced by construction itself but also with waste and by-products produced in other areas of industry, transforming them and using them in the production of alternative construction materials. Using these materials should be one of the approaches adopted to reduce the environmental impact of the construction industry's production chain, mainly in terms of consumption of natural resources.

The growing awareness of environmental problems has put pressure on the sustainable development of this industry, by using a more rational construction methodology and with a better management of architectural heritage. The construction industry currently faces the challenge of conciliating its production with the conditions required for the sustainable development that are less harsh on the environment.

The sustainability of the construction industry is a very important issue, as it should try to optimise its production cycle whilst taking into account materials such as energy and keeping them within thermodynamic limits. The waste produced should always be reused and/or recycled whenever possible, and that which cannot be reused should be sent to landfills, without posing a threat to the environment.

The ISO 14001 standards on environmental management provide the construction industry with the elements required. These can be integrated with other management requirements with the aim of achieving both environmental and economic objectives.

18.2 The Construction Industry

18.2.1 The Environmental Impact of the Construction Industry

Construction is an activity that exists in all parts of the world that are occupied by man, from cities to the countryside and even amongst forest dwellers.

Generally speaking, the environmental impact of the construction industry is proportional to its social obligation. Population growth, along with the development of industrial activity, enabled improved living conditions and led to increased demand for homes and building better infrastructure.

Both the positive and negative impacts should be considered whilst trying to balance environmental concerns with the construction industry. As well as the negative impact of destroying the landscape's flora and fauna, there are also other very important effects to consider, caused by the consumption of natural resources (raw materials extraction), energy and pollution. However, by incorporating waste from its own activities or by using waste/by-products from other industries in the production of materials/products or infrastructure, the construction industry has a positive impact on the global supply chain, not only reducing consumption of raw materials but also energy [2, 3].

18.2.1.1 Natural Resources

The consumption of natural resources used as a source of raw material for the production of materials/products applied in this sector is proportional to economic and population growth.

The cost of raw materials has started drastically increasing, due to the growth in the global economy, the expansion of foreign markets, as well as an increase in political instability and regional wars [4, 5].

The amount of natural raw materials consumed by the construction industry not only corresponds to their use in producing construction materials, but also to waste resulting from production processes.

Of all natural resources consumed by the population, around 20–50 % are used by the construction sector. With wood for example, an estimated 26–50 % of wood extracted globally is used as a construction material. In spite of being one of the few resources that is renewable, the problem lies in the unsustainable way in which it is extracted.

Based on the current rate, it is estimated that known reserves of some traditional raw materials, such as for example, iron, copper and zinc, will last 79, 31 and 17 years, respectively, and will soon run out [6].

Intensive exploitation of inert products, in particular sand and natural aggregates, from the reserves located around big cities, has led to their depletion, meaning quarries are being increasingly driven further away from cities. This has meant that raw materials have to be transported further, increasing fuel consumption (energy), and therefore their cost, causing also more pollution. On the other hand, increasing environmental control of the extraction of raw materials and the need to make better use of the land surrounding the most populated areas has led to price rises [3].

The consumption of natural resources to produce the materials/products used in the different stages in the life cycle of the construction industry (building, use, etc.) is considerable, with the majority of this corresponding to the building stage. This consumption, in addition to having a geographical impact, depends on the following factors: (a) the amount of waste produced; (b) waste used for the buildings; (c) technology used; (d) maintenance requirements, including any repairs needed to correct any flaws; and (e) useful lifetime.

The use of materials produced using natural resources in the construction industry should be kept to a minimum by incorporating recycled products, thereby reducing the impact on the environment. The amount of recycled material used should be increased, without forgetting that the new materials produced using waste should meet the necessary requirements that apply for its function and should not be of inferior quality compared to materials produced from natural resources.

18.2.1.2 Energy

In industrialised countries, 40 % of energy consumption is used by the construction industry. This figure includes consumption during the construction stage, use of the building including energy for lighting and air conditioning, and the demolition phase [7, 8].

Using waste to produce materials can also reduce energy consumption, as the distance for transporting secondary raw materials is shorter compared to the distance to quarries. Of the energy used to construct a building, around 80 % is used in producing and transporting materials [9]. Some of these materials, namely plastics, aluminium, copper, steel, glass, cement, ceramics, etc., are obtained using energy intensive processes, having a negative impact on the environment [2].

The embodied energy per unit mass of material is not in itself an indicator of its environmental impact, as the different materials present significant differences in terms of efficiency when used for the same purpose, so it is much more important to consider how much material is needed for any particular purpose. Another important factor to consider is the useful lifetime (durability) that the materials offer in different environments. A long useful lifetime may compensate for high energy consumption and vice versa [10].

Energy consumption when buildings are used, mainly for lighting, operating equipment and for air conditioning, can be higher than the energy used during the building stage [10]. This energy consumption can be largely controlled with decisions made by the designer and should be planned during that stage of the project, as the primary sources of energy used are non-renewable, for example, natural gas, oil and coal, etc., besides increasing greenhouse gas emissions. In commercial buildings, especially those with a central air conditioning system, the use of more efficient equipment combined with a suitable frontage can reduce energy consumption by up to 50 % [8].

In order to reduce the environmental impact of energy consumption, for example, reducing greenhouse gases, the EU has been promoting energy produced by renewable sources. Of all renewable energy sources, photovoltaic solar energy has the most potential for the construction industry, as it can be conjugated with city structures, enriching their architectural style. Besides this, there are other advantages, such as great functional versatility, as it can replace other construction materials in buildings, avoid losses in transport and distribution networks (medium voltage) due to production being carried out at the point of consumption, as well as the ability to locally supply energy at peak times.

18.2.1.3 Pollution

The construction industry also produces different types of pollution. The formation of gaseous emissions consisting of toxic gases, CO_2 and dust particles, liquid emissions and solid waste occurs in almost all activities in construction, from the extraction of raw materials to the transportation and production of materials such as cement, concrete, etc., during the usage stage and demolition [3]. The impact due to increased emission of greenhouse gases, namely, carbon dioxide (CO_2), halogen compounds (chlorofluorocarbons—CFC, and hydrofluorocarbons—HFC), methane (CH_4) and nitrous oxide (N_2O), some of which with very long residence times in the atmosphere, is significant not only for ecosystems but also for people, due to the resulting climate change.

The construction industry may be viewed as being one of the largest sources of pollution, particularly due to the production of construction materials. It is the third biggest contributor to CO_2 emissions within the industrial sector on a global level and within the EU [1], representing around 10 % of total CO_2 emissions. Most of these emissions are released whilst producing concrete, the most used construction material in the whole world, made using Portland cement. For CO_2 emissions from concrete production, around 85 % comes from cement production, with the remainder from transporting raw materials and the final product.

The processes for cement and lime production release CO_2, as they involve the calcination of limestone which is a thermal treatment process, in which the following reaction occurs:

$$CaCO_{3(s)} \rightarrow CaO_{(s)} + CO_{2(g)} \tag{18.1}$$

Excluding the CO_2 corresponding to the burning of fuel needed for the process, for every tonne of quicklime produced (CaO), around 786 kg of CO_2 is released into the atmosphere or 595 kg of CO_2 when 1 t of hydrated lime is produced ($CaO{\cdot}H_2O$) [1].

Depending on the fuel and efficiency of the process, producing 1 t of clinker using the dry method produces approximately 820–870 kg of CO_2. Of this, 66 % comes from the calcination of limestone, with some of that absorbed in the carbonation of concretes and mortars [1, 7]. The use of fossil fuels to produce energy generates around 390 kg of CO_2.

During the building work, there are also other aspects, such as the application of asphalt, lead-based paints, etc., or water contamination from cleaning the mixer trucks at the end of the day, that are less significant but also important from a pollution perspective.

In addition to sound pollution, work yard activities also generate particulate matter that can be inhaled and is considered a big source of air pollution. Nevertheless, it is essentially the demolition phase that produces the most dust.

Inside buildings, when they are in use, there is also environmental pollution due to the concentration of some gases formed of volatile organic compounds, pathogenic microorganisms, dust, airborne particles, fibres, etc., released from the ground, materials, cleaning products or from activities involving the use of equipment, in particular the leak of CFC refrigerant fluid used in most air conditioning devices.

The presence of pathogenic microorganisms is usually associated with water produced by infiltration or evaporation related to poor ventilation.

The level of pollution inside buildings can be controlled by the selection of materials, the rate of ventilation (air renewal), particularly the air conditioning systems and ventilation, and the cleaning activities and asepsis.

Materials should be selected based on the amount of volatile organic compounds they release and also the cleaning they require. The most important organic compounds released include formaldehydes, organic compounds from glues, paint, plastics and other organic coatings. Inhalable fibres can come from coatings, such as plaster and stucco, carpeting, thermal insulators, and from the abrasion of pieces containing dangerous fibres, for example, chrysotile, used in the production of asbestos. The effects of these pollutants depend on the type, intensity and exposure time.

18.2.1.4 Waste

In spite of construction being a big cause of environmental pollution, there are many ways in which it can operate as a large-scale recycling industry not only for the waste this sector produces, construction and demolition waste (C&DW) but also waste/by-products from other industries [11–13]. In many developed countries, the constantly rising cost of raw materials and the depletion of natural resources have increased the reuse/recycling of waste as a potential alternative in the construction industry.

Construction consumes a huge range of materials, for example, plastics, plant-based products, different metals, composites, siliceous materials, etc., for different uses and different project types [14]. This fact has encouraged the construction industry to develop and seek alternatives for using waste, including plastics, glass, natural fibres and others, such as aggregates or mixed, promoting the development of new products that have physical characteristics and mechanical properties that are at least similar to conventional materials [15].

In the construction sector, the use of waste/by-products from other industries instead of natural raw materials to build roads, produce cement or alternative building materials that can replace conventional materials, both for economic and environmental reasons, helps reduce pollution and the extraction of natural resources from the Earth’s crust [16].

For example, siliceous materials can be produced with waste that contains silicates in its composition, specifically fly ash from power stations, ash from municipal solid waste incinerators, granulated blast furnace slag and dust from electric arc furnace from steel plants.

The cement industry can also recycle fly ash and granulated blast furnace slag with basic index. Using waste in cement production, for example, replacing 50 % of Portland clinker with granulated blast furnace slag, will not only reduce energy consumption by 40 % but will also markedly reduce the volume of CO_2 released during the production process, thus helping to reduce the greenhouse effect.

The steel sector is also a big recycler of scrap steel in electric arc furnaces, producing steel that can be used to make reinforced concrete. Producing steel in an electric arc furnace consumes just 70 % of the energy needed for production using natural resources and saves natural raw material consumption by around 90 % (iron ore) limiting the amount of waste and CO_2 produced; the production of 1 t of pig iron releases 2.2 t of CO_2.

For the glass industry, the environmental impact of using glass scrap as a raw material for producing glass is smaller, but it does reduce energy consumption by around 5 %.

Finally, in addition to the aspects covered, the use of waste often enables the production of materials with better technical characteristics, as is the case with adding granulated blast furnace slag during cement production, which improves the performance of the concrete against corrosion from chlorides.

18.2.2 Life Cycle Analysis of the Construction Industry

Awareness of environmental problems led society in general to change patterns of consumption, becoming more likely to buy or use products and services that respect the environment, from its production from raw materials to the post-consumer stage.

In order to put into practice a suitable system of environmental management in the construction industry, a systematic analysis of all activities undertaken is required, using analytical tools, such as Life Cycle Analysis (LCA) [17–19].

The ISO standard 14040 defines the principles and framework of LCA. According to this standard, LCA is a relative methodology which compiles the inventory of relevant inputs and outputs associated to a product, process or activity in general, within well-defined limits, and evaluates the potential environmental impacts associated with those inputs and outputs, being the results of the inventory and impact phases interpreted in relation to the objectives of the study [20]. LCA defines emissions into the environment, namely gases, liquids and solids, according to the requirements and guidelines specified in ISO standard 14044 [21]. The requirements and guidelines are dependent from the goal and scope.

The study includes the complete life cycle of the product, process or activity, including the extraction and processing of raw materials, production, transportation, distribution, use, reuse, maintenance, recycling and final disposal of the waste that cannot be processed further for recycling.

In this model, defined as a ‘closed loop’, a ‘cradle to cradle’ analysis is undertaken where all the resources used are optimised, the waste production kept to a minimum, as well as ensuring that the products have an acceptable environmental performance, not intended for landfill but for being used again as raw materials for recycling, creating new products that are identical or different [22].

The construction industry’s working products are buildings and public structures. The stages that constitute the life cycle of this sector range from extraction of the raw materials or transformation of the resources needed for the production of materials that will be used for the whole process, to the construction phase, use during its lifetime, which includes altering and remodelling buildings or repairing and refurbishing constructions, and the (full or partial) demolition stage of the buildings and infrastructure.

Problems associated with extraction, processing and use of raw materials and components used in construction, energy, waste production and environmental effects, as well as the potential reuse of products after their useful lifetime, and recycling and/or waste disposal, will be analysed throughout all stages of the life cycle.

Figure 18.1 shows a block diagram with the life cycle stages of materials in the construction industry, using a ‘cradle to cradle’ approach being the environment the boundary of the system. The blocks are connected by arrows that represent flows of energy and mass.

The input flows (mass and energy) represent the resources that can be extracted from the Earth to support the system. Calculating these input flows provides the information required to analyse the principle of sustainability using renewable resources, which implies that these are used at levels equal to or below those needed for their regeneration.

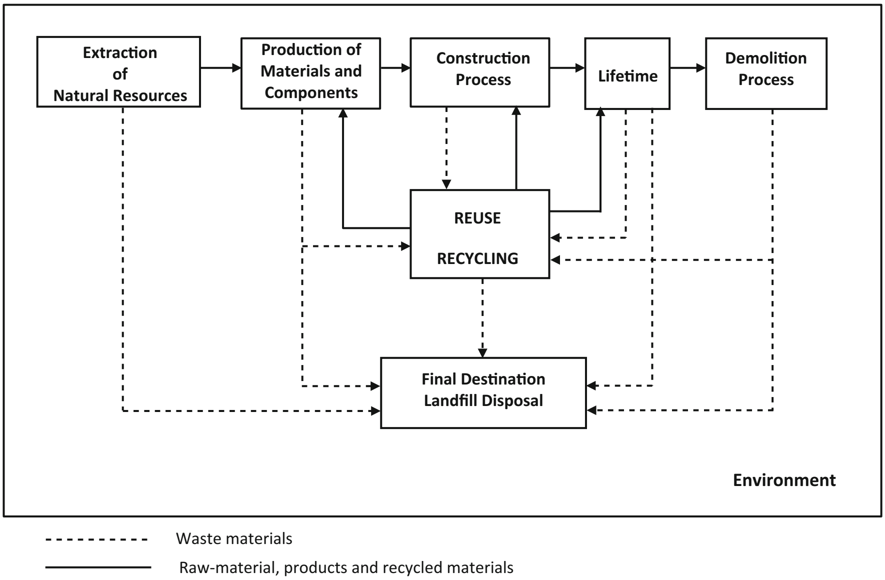

Fig. 18.1 Block diagram showing the life cycle of the construction industry

The output flows are, as well as being the useful product, the energy waste, solid, liquid and gas waste. The quantification of the emissions and waste gives an indication of the effects of pollution associated with the system [23].

The materials extraction phase is significant when assessing the environmental impact of the construction industry, due to energy consumption and use of natural resources for producing materials and products incorporated in this industry.

Interest in the LCA increased with the publication of legislation on environmental control, including integrated pollution control and better production techniques, the growth of the environmentally aware consumer market and the pressure from voluntary associations.

There are different IT tools, such as the SimaPro program [24], that calculate the LCA of processes and products.

In the flow chart for the construction industry, it is important to note the recycling of waste from different life cycle stages, with the recycled materials used again in the construction industry.

The final account of the environmental performance of the construction industry should take into account the waste from construction that can be used in other industries, and the construction industry should also use lots of materials produced using waste from other industries [2].

18.3 Integrated Waste Management

18.3.1 Introduction to Waste-Related Problems

Currently, our society faces many problems associated with environmental management, such as the conservation of natural resources, waste management and reducing the amount of pollutants released into the atmosphere.

In terms of waste, these should not be purely assessed based on the negative environmental impact, as there is also a big economic factor, due to the fact that they can be considered as a source of secondary raw materials.

However, the type of waste management normally used consists of landfill disposal, without any pre-sorting operations, as well as dumping on open land, which is not only bad for the environment but also for public health [25]. Disposal in landfill should be the last option due to the innumerable disadvantages it presents, namely, using and contaminating the soil, impact on ground water, landscape degradation, decreased quality of life and loss of material, causing higher consumption of natural resources [26].

Integrated waste management is one of the emerging holistic approaches to environmental and resource management, based on the concept of sustainable development. Generally, in an integrated waste management system, the treatment options when waste or a product reaches the end of its lifetime are hierarchical, as shown in Fig. 18.2 [27].

The order of priorities for waste treatment operations aims to minimise not only the impact of these on the environment but also preserve the natural resources available [28, 29].

The treatment operations should be analysed as a set of options being used in each situation, those that, through LCA, have a better ‘cradle to cradle’ environmental performance [22, 23, 30].

Besides being a form of pollution, waste also represents a significant loss of resources, which is why full priority should be given to minimising the reduction on the source (prevention and reduction), followed by reusing products. After these options comes recycling (including composting) and energy recovery which includes heat recovery, incineration, as well as other thermal methods, and the

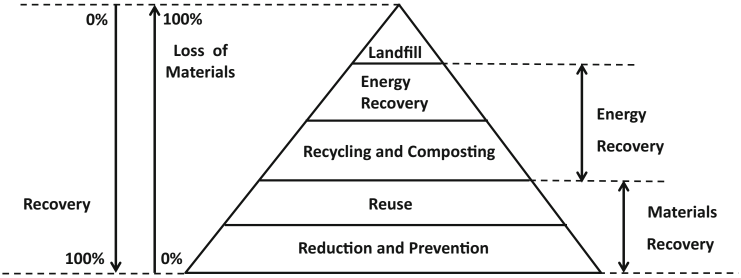

Fig. 18.2 Hierarchy of waste management operations (adapted from [27])

use of landfill gas. Finally, there is the least favourable option for final disposing of solid waste, landfill, due to the loss of the potential value of some components and the fact that it takes up large areas of land [23].

Waste prevention consists of a set of measures which aim to reduce the amount and hazardous nature of materials or substances it contains, both for the environment and for public health.

The concept of waste reduction is not new, and in simple terms, it refers to the strategies and technologies used to reduce waste generation, not including other resources, such as energy, water, etc.; it is sometimes confused with prevention.

Waste production is inevitable because in economic processes, including extraction activities, industrial production and services, there are always losses or waste that produce by-products. Even if the process is optimised, there will be losses and waste. In terms of consumer goods, the lifetime is always limited, turning the product into waste.

Once waste has been produced, the first stage consists of reusing it or reintroducing it into the production/consumption circuit, either being used for the same purpose for which it was originally made or for another use/function without being changed in any way. Reuse has economic advantages, as it reduces the use of materials and energy and reduces the quantity of waste to be disposed of, despite needing the use of logistical infrastructure.

Waste recovery is an option that requires processing (recycling) also requiring industrial infrastructure and logistics with in-built costs. It not only aims to recover materials but also energy (used as a fuel) that can present economic advantages, according to the cost/benefit ratio. Using waste as a raw material reduces the use of non-renewable natural resources and energy to produce materials, and it reduces the end volume of waste, thus reducing the area of land needed for landfill and the costs associated with waste disposal.

The main and most visible environmental contribution of recycling is the preservation of natural resources, which are replaced by waste, prolonging the lifetime of natural reserves and reducing the destruction of the landscape, flora and fauna [31].

Recycling waste is essential for sustainable development, as it closes the cycle of materials (‘cradle to cradle’ analysis), introducing them again in the productive process [22].

Making the decision to recycle waste is something that should be decided on carefully, and all the alternatives associated with using raw materials and energy should be considered, as well as the loss of product quality which may occur during the process, all of which are subject to market laws, with all the constraints that arise from them.

Waste disposal can be done by incineration without energy recovery, permanent storage, for example, in containers in mines, and landfill.

Permanent storage is only a controlled solution that needs a logistical infrastructure, and as well as being costly, it does not offer any kind of waste recovery; it has environmental benefits but no economic benefits.

Landfill represents, indefinitely, the waste of a finite resource, land, space which is increasingly valuable, especially close to large urban centres.

Landfills for hazardous waste concentrated chemical substances at levels that become dangerous and can contaminate the groundwater due to the reaction with the rain water. Many wastes are unstable so landfills pose a risk which remains active for hundreds of years [32].

The different management approaches presented here are not mutually exclusive. As waste is something that is quite heterogeneous, not only because of its origin but also due to the contaminants involved in the production and handling process, sometimes it is more logical to use different solutions for different parts of the waste, reusing the ‘good’ parts, recycling the ‘partially damaged’ parts and incinerating or sending to landfill the very contaminated parts [28].

With the aim of ensuring waste is appropriately treated and promoting whenever possible its recovery in reusable and recycled materials, appropriate legislation has been published by the relevant bodies all over the world.

18.3.2 Legislative Framework

The European Council has had an increasing influence on the management of solid waste, developing various environmental initiatives between 1973 and 1976 with the main aim of controlling and preventing pollution.

In order to ensure protection of the environment and improved quality of life, Directive 75/442/EEC was established on the 15 July 1975, establishing a number of standards with the aim of ensuring not only the disposal of waste but also encouraging waste recovery and reuse in general, to preserve natural resources.

This policy remained in force until 1991, when on the 18th of March the European Council adopted Directive 91/156/EEC which amended 75/442/EEC. This directive aimed to make waste management more efficient through prevention, harmonising legislation at European level, encouraging the reuse and recycling of waste as an alternative to natural resources and ensuring that the European Community and each member state (MS) becomes self-sufficient when it comes to waste disposal.

For the last (VI) environmental action programme (2001–2010), plans were developed for the sustainable use of natural resources and the management of secondary resources (waste), exploring possibilities to reduce waste and the harmful effects of waste. The programme took into account the fact that reuse and recycling processes should be improved, lengthening the life cycle of the materials. It stipulated targets for reducing the amount of waste sent to landfill, 20 % in 2010, aiming for a reduction of 50 % by 2050, as well as making it compulsory for EU MS to establish waste prevention programmes by 12 December 2013.

On 3 May 2000, under Directive 2000/532/EC, the Commission established the European List of Waste (ELW) (previously the European Waste Catalogue—EWC), which covers all types of waste produced in the EU.

The European Parliament and the European Council published Directive 2006/12/EC which revoked Directive 75/442/EEC, adopting the text of Directive 91/156/EEC with almost no amendments.

In 2008, Directive 2008/98/EC was published, on 19 November, aiming to harmonise legislation at European level, clarifying the definitions used and providing a practical application for the hierarchy of waste management. This waste directive established quite ambitious recycling targets for C&DW, stating that in 2020, 70 % of C&DW produced in the MS will be recycled.

Some EU countries have created regulations and taken initiatives to promote the correct management of this particular waste stream, in order to guarantee environmental protection.

Several countries in Western Europe, namely Germany have introduced C&D waste management in their legislation, after implementing the EWC which entered in force on 1 January 2002. The demolition contractors have a special responsibility in the C&DW management process, recovering and processing end of life materials and reintroducing waste into the construction market [33].

Legislation in the United Kingdom related to the integrated management of C&DW includes the use of this waste not only in construction but also for the production of aggregates [33].

In Scandinavia, the management of C&DW is very similar with the policies that have been adopted by the Western European countries. In Denmark, the municipalities are responsible for collecting C&DW, having more than half of introduced specific regulations on the sorting of this particular waste stream [33].

In Southern Europe, the situation regarding C&DW management is more complicated. In Portugal, the construction industry does not have a tradition of reusing or recycling the waste it produces, with most of it going to landfills or being disposed of illegally [34]. Legislation for regulating the production and management of C&DW stream was approved in 2008 and was very important not only for the large quantities produced of this specific type of waste but also due to the frequent illegal disposal of C&DW which has to be stopped.

The legal system for waste management was approved in Portugal for the first time through Executive Law no. 488/85, which encouraged reduced waste production, the development of technological processes for waste recycling and the removal of non-recycled waste, using their energy potential.

With the publication of Executive Law no. 239/1997 of 9 September, regulations were established for national waste management, with the disposal of waste in landfill regulated by Executive Law no. 52/2002 on 23 May.

In 2004, Directive 2000/532/EC on the ELW was replaced in Portuguese law by Ordinance 209/2004 of 3 March.

With the publication on 5 September of Executive Law no. 178/2006, which instituted the general law on waste management, Executive Law no. 239/1997 was repealed. Executive Law no. 178/2006 defines C&DW as waste from the construction, rebuilding, extension, alteration, conservation, demolition and collapse of buildings.

In spite of the legislation applied to waste management since 1985, the first specific regulations on managing C&DW were only published in 2008, through Executive Law no. 46/2008 of 12 March, which included prevention, reuse and collection, transportation, storage, sorting, treatment, recovery and disposal. However, whenever there is some point on C&DW management that is not specified in the aforementioned executive law, the relevant executive law on waste management is applied.

Producers and managers of C&DW should comply with the legal provisions which apply to the specific waste stream contained in the C&DW, specifically packaging waste, waste from electrical and electronic equipment, used oil, used tyres and waste containing polychlorobiphenyls (PCB).

Responsibility for managing C&DW defined in Executive Law no. 46/2008 is attributed to:

1. All stakeholders involved in the life cycle, from the original product to the waste produced, in accordance with the involvement they have.
2. Producers of C&DW (project managers and contractors), for buildings subject to licensing or prior notice under the legal terms of urbanisation and construction.
3. Bodies responsible for managing municipal solid waste (city councils), in the case of private projects without a licence or prior notice under the legal terms on urbanisation and construction.
4. Holders of C&DW, when it is not possible to identify the producer of these.

However the responsibility for managing the C&DW of the aforementioned bodies ends with:

1. The C&DW is delivered to facilities or those in charge of waste management who are duly licensed.
2. Responsibility is transferred to bodies responsible for managing waste flows.

This executive law also regulates the following actions:

1. Hierarchy of management for C&DW which prioritises reuse of C&DW in construction followed by sorting on point of origin of C&DW. If sorting is not possible at the point of waste production, it can be undertaken at a site involved with the project. Based on the hierarchy, C&DW is sent to licensed operators for this purpose.
2. Compulsory sorting prior to disposal of C&DW in landfill.
3. Use of C&DW in construction provided it meets the requirements of the national or European technical standards.

On 17 June 2011, Executive Law no. 73/2011 was published, which amends the general law on waste, and Directive 2008/98/EC was enforced on 19 November by the European Parliament and the Council. This executive law considers it a priority to prevent the production of waste and promote reuse and recycling, with the aim of prolonging its use in the economy before returning it to nature. Furthermore, it is considered important to promote the full use of the new organised waste market (OWM), as a means of consolidating the recovery of waste, with advantages for economic agents, as well as stimulating the use of specific waste with a high recovery potential.

Outside EU, in the United States, C&DW management is not covered by federal legislation since most materials constituting these residues are not considered hazardous material. Legislation varies across the states according to their characteristics, namely, annual rainfall and temperature range, land availability, geologic stability and policy related to the risk that C&DW can create on human health and the environment. This legislative autonomy has led to contradictory regulations throughout the nation. Twenty-three states have specific landfills for C&DW separated from MSW; in other states, landfills for C&DW are the same as inert debris landfills, non-MSW or MSW landfills or general solid waste facilities [35].

In Japan, the Construction Material Recycling Law requires sorting and recycling of specified materials (wood, concrete and asphalt) of C&DW. If a company wants to work in the demolition business, it should be registered by the prefectural government [36].

18.4 Construction and Demolition Waste

18.4.1 Introduction

The construction industry is considered the biggest producer of different types of waste, of all of society, with C&DW representing almost 31 % of all waste produced in the EU [37].

The source of construction waste varies a lot. Waste may come from construction losses or changes to buildings, from demolished buildings and asphalt streets, from disasters involving building collapse or damage, from excavation and clearing of land or from natural disasters, and as a result, it is very heterogeneous [38].

In any production process, there is always a certain volume of waste that is associated with the technological characteristics of the process. When the amount of loss is over the typical minimum limit for the technology used, it is considered to be waste. For the same technology, the amount of loss varies with regional characteristics and also time, so it is difficult to establish a set figure associated with the process and the wastage [39].

Loss occurs at different stages of the construction industry life cycle. The project stage is fundamental, as choosing inappropriate technology can increase the amount of waste, as can overestimating the size or building a structure that is not needed. Nevertheless, losses caused by inadequate planning are only apparent during the construction stage.

In renovation work, the amount of waste produced is associated with the lack of a culture of reusing and recycling C&DW as a construction material and not due to the waste of materials.

In demolition work [40], the amount of waste produced can be predicted and is not directly related to the processes used or the quality of the sector. Nevertheless, the quality of the waste can depend indirectly on technology, the construction processes and the system of demolition used. Some construction and demolition systems can produce waste with greater potential for recycling, compared to others that consist of mixtures of materials and components where contamination may make reusing or recycling them difficult. Another problem associated with waste is its volume, giving an increased cost of treatment and deposition, especially of waste that is classified as hazardous.

There is no standard classification or statistics for waste in this sector, but the levels of waste in the construction industry are very high and depend on the intensity of the construction work in each country, the technology used and the rates of waste and maintenance required, making it difficult to draw comparisons.

The average levels of loss provide an estimate of construction material waste. Comparing the estimated mass of the building with the mass of the materials acquired to build it, it is estimated that around 20 % is wasted. Of the material wasted, approximately half is used in the construction process itself and the other half leaves as waste [41]; the materials that are rejected from construction work may be considered as ‘urban mines’ of raw materials.

Managing waste costs money; these costs are first associated with their removal and transportation and secondly related to buying the material needed to make up for losses and also for paying surplus labour costs, etc.

In Western Europe, around 80 % of all C&DW comes from maintenance and demolition work and the remainder from construction work [31]. According to the Environmental Protection Agency (EPA), in 2003, in the United States, 47 % of waste came from construction work and refurbishment and 52 % from demolition [42]. These figures not only reflect the relative importance of construction work, maintenance and demolition work for each economy but also the rate of loss of materials in both areas of construction work.

In 2005, the average production estimate of C&DW in the EU was 290 million tonnes, corresponding to 480 kg per capita per year, whilst for MSW, it was 390 kg per capita per year [43, 44]. The C&DW produced equates to 22 % of the total waste produced and is the biggest flow of waste in quantitative terms excluding waste from mining and agricultural activity. Of the total C&DW, 60 % is from earth from excavation and levelling work, this means that this waste does not need treating (apart from earth that is contaminated) [45].

In the United States, figures supplied by the EPA suggest an increase from 136 million tonnes of C&DW produced in 1998 to 164 million tonnes in 2003. The per capita production of C&DW in 2003 was 463 kg per year, whereas MSW was 720 kg per capita per year. This disparity in the rate of production of waste per capita in the North American economy can be attributed to lower waste production in construction activities or even to the smaller role of construction in the North American economy (4 % of GDP) [42].

In Portugal, in 2005, C&DW production was around 7.5 million tonnes per year with a per capita production of 325 kg per year [46]. As with other EU countries, this figure corresponds to around 22 % of the total volume of the country's waste. Most of this waste (95 %) is sent to landfill, taking up a bigger area than MSW [47]. The construction sector represents 4.9 % of the GDP.

The figures on the production of different types of waste vary depending on the bibliographical sources used. In the case of C&DW, the figures show a larger discrepancy, as sometimes the figures concerning this specific waste do not include the figures for excavation waste, asphalt and clearing vegetation.

Natural disasters or wars are other factors that can cause a significant increase in the volume of waste.

18.4.2 Waste Classification

The first waste classification was legally established by the EU in 2000 with the ELW. This list defines and classifies all waste produced in the EU, identifying those that are considered hazardous.

Waste is considered hazardous if it has properties that make it dangerous or pose a threat to public health or the environment. The factors considered in this classification include toxicity, flammability, corrosiveness, reactivity, pathogenicity, radioactivity, etc.

The ELW consists of 20 chapters essentially grouped by the type of activity and divided into classes and subclasses. Waste is defined with a six digit code, with each two digits representing the chapter, the subchapter and the type of waste.

C&DW is classified in the ELW with the code 170000, with the last four digits representing the type of C&DW analysed, as shown in Table 18.1 [Directive 2000/532/EC and Ministerial Order no. 209/2004 of 3 March].

As well as this classification, C&DW can be generically classified according to the type of work that gave rise, the type of material, how hazardous the components are and the final treatment it can be undergone [48], as shown in Table 18.2.

18.4.3 Characterisation of C&DW

The construction industry has accompanied the development of materials, incorporating them in projects, so the composition of C&DW has been changing over time.

For example, fibre cement or insulation materials used in older buildings contained asbestos, and they can no longer be used in construction because of their toxicity.

Table 18.1 Legal classification of C&DW [Directive 2000/532/EC and Ministerial Order no. 209/2004 of 3 March]

Code 17	C&DW (Including road building and excavated soil from contaminated sites)
17 01	*Concrete*, *bricks*, *tiles*, *roof tiles*, *ceramics and gypsum-based materials*
17 01 01	Concrete
17 01 02	Bricks
17 01 03	Tiles, roof tiles and ceramic materials
17 01 04	Gypsum-based construction materials
17 01 05	Asbestos-based construction materials
17 01 06[a]	Mixtures of, or separate fractions of concrete, bricks, tiles and ceramics containing dangerous substances
17 01 07	Mixtures of concrete, bricks, tiles, roof tiles and ceramics other than those mentioned in 17 01 06
17 02	*Wood*, *glass and plastic*
17 02 01	Wood
17 02 02	Glass
17 02 03	Plastic
17 02 04[a]	Glass, plastic and wood containing or contaminated with hazardous substances
17 03	*Bituminous mixtures*, *coal tar and tarred products*:
17 03 01[a]	Bituminous mixtures containing coal tar
17 03 02	Bituminous mixtures other than those mentioned in 17 03 01
17 03 03[a]	Coal tar and tarred products
17 04	*Metals* (*including their alloys*):
17 04 01	Copper, bronze and brass
17 04 02	Aluminium
17 04 03	Lead
17 04 04	Zinc
17 04 05	Iron and steel
17 04 06	Tin
17 04 07	Mixed metals
17 04 08	Cables
17 04 09[a]	Metal waste contaminated with dangerous substances
17 04 10[a]	Cables containing oil, coal tar and other dangerous substances
17 04 11	Cables other than those mentioned in 17 04 10
17 05	*Soil* (*including excavated soil from contaminated sites*), *stones and dredging spoil*
17 05 03[a]	Soil and stones containing dangerous substances
17 05 04	Soil and stones other than those mentioned in 17 05 03
17 05 05[a]	Dredging spoil containing dangerous substances
17 05 06	Dredging spoil other than those mentioned in 17 05 05
17 05 07[a]	Track ballast containing dangerous substances
17 05 08	Track ballast other than those mentioned in 17 05 07
17 06	*Insulation materials and asbestos-containing construction materials*
17 06 01[a]	Insulation materials containing asbestos
17 06 02	Other insulation materials
17 06 03[a]	Other insulation materials consisting of or containing dangerous substances

(continued)

Table 18.1 (continued)

Code 17	C&DW (Including road building and excavated soil from contaminated sites)
17 06 04	Insulation materials other than those mentioned in 17 06 01 and 17 06 03
17 06 05[a]	Construction materials containing asbestos
17 07	*Mixed construction and demolition waste*:
17 07 02[a]	Mixed construction and demolition waste or separated fractions containing dangerous substances
17 07 03	Mixed construction and demolition waste other than those mentioned in 17 07 02
17 08	*Gypsum-based construction materials*
17 08 01[a]	Gypsum-based construction materials contaminated with dangerous substances
17 08 02	Gypsum-based construction materials other than those mentioned in 17 08 01
17 09	*Other construction and demolition waste*
1709 01[a]	Construction and demolition waste containing mercury
17 09 02[a]	Construction and demolition waste containing PCB (e.g. PCB-containing sealants, PCB-containing resin-based floorings, PCB-containing sealed glazing units, PCB-containing capacitors)
17 09 03[a]	Other construction and demolition waste (including mixed wastes) containing dangerous substances
17 09 04	Mixed construction and demolition waste other than those mentioned in 17 09 01, 17 09 02 and 17 09 03

[a] Dangerous substances

In the 1950s and 1960s, lead in pipes was replaced with copper, and with the large influx of workers to major urban centres, construction using reinforced concrete became widespread.

More recently, in the 1980s, with the widespread use of plastics in residential buildings—such as polyethylene (PE), polyvinyl chloride (PVC) and polystyrene (PS)—plumbing and door/window frames have also started to be made of PVC, and industrial and service buildings have begun to be built using steel structures. The lower fire resistance of these structures led to the need to protect the beams and pillars and install firefighting equipment made of materials that contain halogen elements and other dangerous chemicals.

Currently, parking garages built in building basements have led to an increase in the volume of soil and rock removed, which has become part of construction waste. The growing use of glass in office building and shopping centre façades will affect the composition of demolition waste in the future.

Human (sabotage or terrorism) or natural disasters (hurricanes, tornadoes, earthquakes) produce a mixture of waste that it is not possible to separate, such as asphalt roofs, linoleum flooring, dangerous materials, specifically asbestos, concrete (with and without metal reinforcement), filler material (earth, gravel, sand), miscellaneous material as well as demolition material. The heterogeneous nature of this waste means it cannot be sorted, so the materials cannot be reused or recycled.

Table 18.2 General classification of C&DW

Classification	Characteristics
Type of work	• *Construction waste*: waste from new construction works for buildings and infrastructure
	• *Demolition waste*: waste from demolition of buildings and infrastructure
	• *Repair work waste*: waste from refurbishment and repair of buildings and infrastructure
Type of material	• *Waste from structural concrete* (simple or reinforced)
	• *Waste from masonry*
	• *Waste from asphalt materials*
	• *Waste from vegetation and unwanted soil*
Dangerous nature (of this material)	• *Inert waste*: this includes waste from concrete, soil, mortar, bricks, roofing tiles, masonry, etc.
	• *Non-inert waste*: this includes waste from different packaging, plastics, wood, metal, glass, etc.
	• *Hazardous waste*: this includes waste from asphalt, used oil, tins of paint and solvent, asbestos, etc.
Final destination	• *Reusable waste*: waste that can be reused directly on the work site or on another, consisting of clean bricks, concrete blocks, stone façades, roofing tiles and metal, vinyl coating, wooden cupboards, balconies, stairs, piping/electrical equipment, carpets, clean insulation and wooden/front beams
	• *Recyclable waste*: waste that can be recycled, consisting of broken bricks, concrete or stone façades, ceramics and tiles, damaged or broken glass windows, wooden beams, trees, metal dividers, covering material, aluminium window and door frames
	• *Non-recyclable waste*: waste that, either due to its characteristics or because it is contaminated, cannot be recycled, particularly mixed waste that cannot be sorted, non-recyclable materials, such as asphalt, linoleum flooring, dangerous waste including asbestos, treated wood waste (cladding or door frames) wood shavings and wood contaminated by paint

Building road infrastructure has led to greater amounts of asphalt in waste, because of its use as a binding material for the aggregate particles in road surfaces and also as a waterproofing material in emulsions and bitumen membranes, thanks to their hydrophobic characteristics. This waste basically has the same composition as waste from disaster situations, further including more varied materials, such as already separated reinforcing metal, metal signs and road dividers.

The composition of C&DW depends on geographic location and varies from country to country. It depends not only on the materials used in building but also on the stage of development of the industry, that is, the quality of the labour force, the construction techniques and the use of quality control techniques in the production process, so it is very difficult to give a single profile for its composition.

According to Henrichsen [49], C&DW consists of 50 % concrete (simple or reinforced), masonry and mortar and 20–25 % excavated soil, gravel for flooring restoration, asphaltic material and other less significant materials.

Nonetheless, in Portugal, the part related to excavated soil and gravel of flooring restoration represents 40 % (weight) of C&DW, the percentage being higher than the concrete, masonry and mortar part (35 %), contrary to the results presented by Henrichsen. Further to these parts, there are also some significant parts consisting of asphalt (6 %), mud from dredging and drilling (5 %) and metals (5 %) [34, 50].

In both studies, the inert part of C&DW represents at least 2/3 of all waste produced.

The fraction corresponding to inert material is considered the most important, because of its chemical and physical characteristics and its potential for recycling. This fraction is composed essentially of concrete waste from demolitions and consists of concrete made of hydraulic cement, whose weight composition is at least 95 % of concrete, a maximum 5 % petreous material and 1 % bituminous material, in the form of coarse aggregate (material with a particle size between 38.1 mm and 4.75 mm), fine aggregate (particle size less than 4.75 mm) and cement paste. Concrete represents around 75 % (weight) of all construction materials and is responsible for the largest proportion of waste from demolitions. As well as this fraction, C&DW contains other non-inert mineral materials such as chlorides, sulphates, organic matter and lightweight industrial products (paper, plastic, cloth, rubber, etc.), steel, aluminium, iron, glass, etc. It may also contain plaster and other material such as soil, mixed material and vegetation waste from earthworks or clearing land and building works.

In terms of masonry waste, there are several types, according to the level of purity, and it is predominantly composed of blocks, bricks, clay pieces, roof and wall or floor tiles, glass, etc.

The composition of C&DW in Europe is very different to the composition in the United States. In the United States, the wood content (treated and untreated) in the mass of construction waste is around 30 %, followed by covering materials (20 %), and blocks of masonry and concrete, between 1 and 8 % for residential buildings and 10 and 20 % for commercial buildings. Green waste counts for the smallest percentage (2 %) [49].

Compared to other types of waste, the volume taken up by C&DW is large, but as it is normally considered inert, it does not create concern for public or environmental health because of leaching from its components, the propagation of toxic materials or problems with organic matter rotting, as is the case for municipal solid waste (MSW). There is little data in literature about the individual nature of each of the components of C&DW that may cause damage to the environment or lead to degradation of a new product and also on the synergy between components that may potentially contaminate the environment.

However, the classification of C&DW may be altered because of its heterogeneous nature and the relationship between its characteristics and the work that produced them; in other words, a particular work may produce inert waste, whilst another may have components, such as adhesives, paint, oil, batteries, biocides in treated wood and asbestos, that make the waste less inert or even dangerous. The chemical analysis of leachates from landfills has shown quantities of toxic substances that are higher than the limits established in legislation.

C&DW has variable physical characteristics that depend on its generation process and may have the shape and size of the building materials (such as sand or gravel), or irregular sizes and formats, such as pieces of wood, mortar, concrete, plastic, metal, etc. Waste from demolition work has, in theory, a larger particle size than waste from construction processes, which are formed mostly of finer components.

In spite of its heterogeneous nature, the vast majority of C&DW components have high mechanical strength, whereby studying the physical and chemical properties of C&DW is fundamental to using it as a secondary raw material to optimise the properties of the new materials.

18.4.4 Ecotoxicological Effects of C&DW

C&DW may have a negative effect on public health and the environment if it contains dangerous components, such as asbestos, lead-based paint, coverings, adhesives, resins, plasterboard and tar creosote.

Lead-based paint aims to increase durability and speed up drying time. Contact with this type of paint can cause damage to the nervous system and cause developmental delay.

Tar creosote is used to preserve wood exposed to outdoor. Ingesting large quantities of creosote can cause mouth burns and stomach pains. If it comes into contact with the skin, it can cause irritation.

In the civil construction industry, asbestos has been used to increase the mechanical strength of cement and plastic, for insulation, fire protection and sound insulation. Asbestos is a group of natural minerals made of hydrated silicate and is composed of long, fine fibres that can be easily inhaled by humans. Regular exposure to asbestos can cause illnesses like asbestosis, mesothelioma and lung cancer, amongst others. Recognising the danger to public health posed by asbestos led to a decrease in its use during the second half of the twentieth century.

The problems with asbestos are related to eliminating it. The problem of the risk to public health is decreasing because the waste that is considered dangerous is being removed before buildings are demolished.

In the EU, in accordance with the ELW, asbestos is classified as dangerous waste and must be processed at special waste treatment facilities. The use of asbestos has been banned in the EU since 2005.

18.5 Recovery of C&DW

18.5.1 Introduction

The reuse of waste in the construction industry has existed since ancient times (the Roman Empire and Ancient Greece), where materials from demolished buildings were used to build new ones. Leftovers from tiles, bricks and lumps of ceramic were used without any treatment (with a large particle size) to produce rudimentary concrete or were milled and used as binders, taking advantage of the pozzolanic properties of ceramic materials.

In Germany, in the nineteenth century, the remains of concrete blocks were used to make artefacts. In Europe, following the Second World War, construction waste was recycled, since the demand for building materials was greater than reserves at the time.

In the last decades of the last century, economic and environmental reasons, such as the depletion of natural inert materials, led to several countries adopting specific policies to effectively recycle C&DW, since they can substitute to a large extent the natural inert materials used to produce concrete, blocks and flooring bases. Nonetheless, there are still great disparities in the application of these measures between different European Union countries.

Sorting of construction waste is a fundamental operation in recovering them, through reuse and recycling. Management of waste by the builder, as well as showing environmental responsibility, is also economically advantageous, since it makes possible to reduce the costs from processes and products.

The construction sector, for the extraordinary physical volume of materials that it involves, is potentially the largest market for the reuse and recycling of C&DW, providing a larger economy of natural resources (raw materials and energy) and minimising impact on the environment, as well as encouraging greater sustainability. On the other hand, the possibility of this sector to be a route to explore the sealing of dangerous industrial waste has been considered, since a large number of construction products do not come into direct contact with the weather, which limits its effect on the environment [51].

Recycling waste will introduce alternative products to the market for the same function and perhaps more appropriate solutions for specific situations, with gains in the overall efficiency of the process. In this way, reducing the costs of producing an appropriate material for many applications in civil construction may help to reduce the costs of housing and road infrastructure, railways, dams, etc.

These new products have found several legal/regulatory, technological, economic, geographic and information barriers, not only from consumers but also from technicians, since it is commonly stated that the quality of products containing waste is inferior. This problem can only be overcome by long-term policies.

The difficulty in introducing new technology to civil construction is real. The impact made on the real estate work costs is small, due to the price of land and the existence of prescriptive standards that specify the use of a particular solution rather than a product’s performance. The economic problem can be more easily overcome using technology, by developing products with competitive advantageous over traditional ones, and legally, by (a) using legislative actions that encourage market creation; (b) making it compulsory for a minimum amount of recycled material to be used in the production process of a specific product; (c) increasing the tax on waste disposal; and (d) reducing the cost of recycled products, through tax breaks for products containing waste or other incentives or risk sharing.

These measures were put into practice in the United States through the EPA, which defined the minimum waste content to be incorporated in production processes, for example, on the production of Portland cement (15 % fly ash and 25 % blast furnace slag). In the United Kingdom, studies are underway that aim to define the minimum waste content in the composition of certain materials and the introduction of improvements in the market of products containing waste, imposing a tax on all material sent to landfills, as well as making long-term contracts possible for waste recycling.

The existence of certification systems for products, from the point of view of technical and environmental performance, is one of the measures to be implemented to overcome the technical resistance faced by products containing waste.

Introducing new products to a sector as conservative as construction, which has little experience in technological innovation, must be done according to a carefully defined marketing plan. Financial viability is fundamental to every stage, since many products, although technically viable, never make it to the market because of financial viability. This factor should bear in mind the product's market value, which includes the costs of the recycling or landfilling processes.

18.5.2 Recycling Materials Contained in C&DW

Integration of C&DW in the production chain is done by recycling. Recycling plays a significant role in the economy, increasing its competitiveness, creating new business opportunities and even creating jobs, since it makes it possible to generate value from a product that was considered an expense.

Optimising this operation is, fundamentally, the result of selective collection of materials depending on their characteristics and nature.

The recycling rate for C&DW varies greatly from country to country, since it depends on factors such as the availability of natural resources, the economic and technological situation of the country and the distance to natural raw materials.

In 1990, the recycling rate for C&DW was an average of 28 %, but its value has grown. However, in some EU countries the rate is already high, specifically in Denmark 90 %, Germany 83 % and Holland 87 % [52], thanks to special initiatives, such as the landfill tax created in Denmark in 1990.

The environmental impact of recycling activities is not always satisfactory, since it depends on many different factors, such as the type of waste and the technology used. If these factors are not appropriate, it may be necessary to use energy and even raw materials to transform the waste, which could make the recycling process expensive.

The potential for recovering C&DW is high provided that it is properly managed, and up to 80 % may be recycled [53]. Although there are many material recycling systems, recycling C&DW is restricted to only some types of waste.

Recycling waste allows in most cases a reduction in energy consumption in producing a certain product, because often the materials already include energy, which is true for recycling steel, aluminium and also for blast furnace slag. Other times, partially organic waste may be a source of energy, as well as increasing the mass of the final product. This is the case for rice husk, which contains around 20 % ash that is predominantly silicon- based.

Disposing of waste in a landfill involves an increase in energy because of transport and managing the landfill.

During the construction stage, with the aim of avoiding the contamination of materials to be recycled, appropriate areas should be made or containers installed to separate the different materials to be treated.

During the demolition stage, separating and cleaning the waste can be made more efficient if done carefully, by hand, and piece by piece. This procedure requires a great amount of time, space and labour force, so faster demolition systems are normally adopted, giving rise to large quantities of waste composed of a mixture of material with different origins and characteristics.

Selecting a viable alternative for the recycling process is only possible with detailed knowledge about the waste, which includes an exhaustive characterisation of the chemical and microstructural composition, as well as the characteristics of the process that produced it and respective environmental impact.

The different materials that make up C&DW, because of their different characteristics, do not undergo the same recycling operations. For each type of waste, there are many technically viable recycling routes, and it is important that there are rules to simply identify the different options, not using preconceived ideas but rather the combination of objective characteristics of the waste and the requirements of the different applications.

The option chosen should be the one with the greatest market potential and that minimises environmental impact. At this stage, the decision is made using a more qualitative than quantitative analysis.

Metallic materials, such as steel, copper, aluminium, iron, brass and zinc, can be easily recovered and reintroduced into the production cycle without losing their properties.

Cardboard and paper, provided that they have not been contaminated with impurities, can be introduced into the respective production processes and can also be used in the manufacture of cellulose-based insulation.

Recycling plastics, provided they are separated, poses no problems. Nonetheless, recycling plastics is more problematic when they are mixed or combined with other materials to form composites.

Glass is easily recycled and is integrated into the glass manufacturing process. The only problem is that different coloured glass cannot be recycled together.

18.5.3 C&DW Recycling Plants

The operations and equipment used in C&DW recycling processes are very similar to those used for processing ores.

The fundamental unit operation is fragmentation, followed by the unit operations of sieving and magnetic separation.

Due to the heterogeneous nature of the waste, specifically in terms of size, waste is crushed, normally in successive stages, whereby particle size is gradually reduced until the materials are freed, and a material with the desired size is obtained. For economic reasons, it is normally desirable for the material to be crushed only once, and a material with a wide range of particle sizes is obtained, that is, the diameter of the particles varies from very small sizes to sizes of more than 50 mm.

The most commonly used crushing equipment includes jaw crushers, cone crushers and hammer mills. This equipment applies compressive, impact and abrasive forces to reduce the size of the waste particles and liberate the different components so they can be separated and recovered in other operations.

Jaw crushers are normally used as primary crushers, since they do not reduce very much the size of the materials and generate a large amount of coarse aggregate. The particles break because of the compressive forces applied. Generally, the processed material is subjected to further fragmentation by smaller jaw crushers or hammer mills.

The disadvantages of that type of equipment lie in the fact that they are very noisy, produce a large amount of coarse material and beams and pillars produce low-quality lamellar particles because they have very pronounced fracture lines that may produce weak points. It is difficult to break down reinforced parts, and it is almost impossible to fragment large-scale wooden pieces, since they normally cause the axes of the crusher to break.

This type of equipment is most appropriate for processing structural concrete waste, since it makes it possible to obtain recycled material with good particle size characteristics for use in concrete. It has the advantage of having low maintenance costs.

Cone crushers are the most commonly used because of their robustness; they process reinforced concrete pieces or wooden beams, applying low compressive and impact forces. They greatly reduce the size of the waste, producing considerable quantities of fine and coarse aggregate. Cubic particles with good mechanical characteristics are found, since the particles break along natural rupture lines.

Although they are not noisy, they are disadvantageous because of their high maintenance costs. It is the most suitable equipment for producing recycled material for use in flooring.

Hammer mills are used as secondary crushers and are normally used together with jaw crushers. They generally have a mesh at the output end, which stops larger particles from leaving the impact chamber. This mesh can be replaced by meshes with different sized openings, so that material with different particle sizes can be obtained.

The rupture system of particles is similar to that when the cone crusher is used, that is, the particles break along natural rupture lines, producing a large amount of fine particles.

In terms of collection and treatment of waste, there are two methods. In one, the waste is separated selectively by the type of material and undergoes pre-crushing at the site where it is produced, using mobile equipment. In the other method, the material is demolished and removed from the work site in a nonselective way and without any prior treatment and is later transferred to companies in the recycling sector, which take on responsibility for treatment of the material. In this case, the equipment is fixed.

The operations of a C&DW recycling plant include the following steps:

1. Receiving the C&DW
    - This stage involves a visual inspection and weighing on a weighbridge.
2. Sorting at the plant
    - In the case of reinforced concrete, the steel is separated from the concrete using a hydraulic hammer and clamp crushers and are then sent on for recycling.
    - The C&DW is subjected to checks for possible contamination, separating the contaminated material from non-contaminated material, because if contamination is found, it will affect the following stages.
3. Forwarding non-contaminated C&DW
    - Materials such as concrete, brick, ceramic or mixture of concrete, masonry and stone are sent for primary sieving, whose aim is to remove the pieces measuring 0–5 mm, which is normally formed of particles of plaster, organic matter and dust, and it is then sent for crushing.
4. Forwarding contaminated C&DW
    - Elements, such as wood, paper, metal, insulation, etc., are removed by hand or with the help of pincers, for example.
    - Afterwards, they are sent to the sorting unit, with vibrating sieves and magnetic separation.
    - Lastly, before being sent for crushing, the waste passes through a primary sieve, with the aim of removing pieces measuring 0–5 mm.

5. Crushing with sieving and magnetic separation

   - Crushing is performed by impact or jaw crushers, and the output material has a particle size between 0 and 80 mm. At the output from the crusher, the material passes through a magnetic separator to remove the remaining metal.

6. Storage

   - Materials are separated according to origin and main components.
   - Protection against the weather.
   - Avoiding segregation of materials.

The capacity and complexity of a recycling plant depend on the supply of waste and the demand for recycled inert material, as well as the characteristics desired for the product.

Recycling plants should be located as close as possible to urban centres, not only so that they are close to the sites that produce waste but also to be close to the users of recycled aggregate, thereby reducing transport costs and the costs of producing recycled materials. However, being located in urban areas may cause problems due to noise and dust emissions, causing resistance from local residents. These problems may be minimised, however, by adapting the equipment.

As the quality of recycled inert material depends on the quality of the original material and because waste is very heterogeneous, during processing, it should be subjected to a homogenisation operation.

As well as using suitable demolition techniques and carrying out a preselection of supply material, recycling equipment should be flexible and be prepared for a large variation in the materials' properties.

Material impurities should be removed manually before and/or during crushing, and ferrous metals should be separated using electromagnets. In the second sorting operation, lighter material is separated, followed by a second fragmentation and sieving. Finally, finer sorting is performed, either wet or dry, in order to remove friable particles, organic matter and other fine impurities, etc.

Using impurity separation techniques may increase dust emissions and generate new waste, whose final destination may increase the production costs of the recycling units.

This way, two types of waste processing can be used, either wet or dry, with dry waste processing plants being the more common of the two [54].

The equipment used in wet processing is more sophisticated and produces better quality inert material. In wet processing, further to the stages used in the dry method, there are other procedures designed to eliminate material with reduced specific weight. The water used in this process can be treated, thereby reducing its environmental impact and operating costs.

Wet processing should be used in plants with a high annual treatment capacity and a sufficient supply of construction materials for recycling, which only happens in large urban areas [54]. Initial investment and production costs are much higher than for dry processing.

The main properties of recycled material that are affected by the procedures and equipment used in the crushing process are classification and composition, impurity content, particle size, and the shape and resistance of the particles. For example, depending on the crushers used, the morphology of the particles can be cubic or lamellar and may have fracture lines.

There is no equipment that simultaneously provides optimisation of these properties. Therefore, the demolition and recycling of the waste should be adjusted in order to optimise the results from a technical and economic point of view for each case.

In any environmental management policy, the reuse of C&DW at the work sites that produce it should be encouraged. If this is not possible, the waste should be sent to licensed operators.

In Portugal, in order to properly refer waste and manage it suitably, the Portuguese Environment Agency (*Agência Portuguesa do Ambiente*—APA) has an Information System for Waste Management Operations Licensing (SILOGR) available on its site [46].

The information in that system relates to licences issued by the Ministry of the Environment and Urban Planning and the Ministry of Health, and the information system relating to licences issued by the Ministry of the Economy is being updated. It should be noted, however, that the data available does not replace or prevail over licences/permits issued by the respective licensing bodies.

This computer application's main objective is to facilitate access to relevant data on waste management operations, and after the user introduces the ELW code and the district desired, information is provided on operators licensed to collect the waste in question.

Licensed operators should comply with the legislation, which prohibits disposing of C&DW in landfills without previously sorting materials with a view to recovering them.

To meet the main needs of operators and agents in the sector, the APA makes available technical specifications, defined by the National Laboratory of Civil Engineering (LNEC), on C&DW and respective uses, which cover the most common potential uses in the civil construction sector.

18.6 Uses for Recycled Materials

Replacing traditional materials with materials produced using waste is only feasible when the properties are suitable for performing the function for which they are designed.

The use of C&DW should take place in accordance with the national and European technical standards applicable. In Portugal, in the absence of the abovementioned standards, the technical specifications defined by the LNEC are used, in accordance with Table 18.3 [55–58].

Table 18.3 LNEC technical specifications for the use of C&DW

LNEC specification	Recycled material	Use
E 471-2009 Guide to use of coarse recycled aggregates in the manufacture of concretes with hydraulic binders	• Coarse recycled aggregates	• Filler or blinding concrete, without a structural function, and in aggressive environments • Regular or reinforced concrete
	• Non-bound aggregates, natural stone and treated aggregates with hydraulic binders	
	• Bituminous materials	
	• Floating petreous material	
	• Clay-based masonry elements, calcium silicate masonry elements and non-floating cellular concrete	
E 472-2009 Guide to use of hot bituminous mixtures in plants	• Recycling hot bituminous mixtures in plants	• Wear layer • Base and blinding layer
	• Milled bituminous mixtures	
	• Plates taken from pavement layers, later reduced	
	• Surplus materials from the production of bituminous mixtures	
E 473-2009 Guide to use of recycled aggregates in non-bound road surface layers	• Crushed concretes	• Non-bound road surface layers (base and sub-base)
	• Aggregates from non-bound or cement-treated road surface layers	
	• Masonry	
	• Bituminous mixtures	
E 474-2009 Guide to use of materials from construction and demolition waste in earthworks and the bed layer of transport infrastructure	• Crushed concretes	• Earthworks and bed layer for transport infrastructure
	• Aggregates from non-bound or cement-treated road surface layers	
	• Masonry	
	• Bituminous mixtures	

The LNEC specifications provide recommendations and establish minimum requirements for the use of coarse recycled aggregates in the manufacture of concretes with hydraulic binders (E 471-2009) [55]; for the manufacture and use of hot bituminous mixtures in plants, using recovered bituminous mixtures (E 472-2009) [56]; for the use of recycled aggregates in non-bound road surface layers (base and sub-base) (E 473-2009) [57]; and for recycled materials from C&DW in earthworks and the bed layer of transport infrastructure, specifically roads, airports and railways (E 474-2009) [58].

Coarse recycled aggregates [55] come from construction, rehabilitation and demolition works for buildings or other civil engineering structures and are divided into three classes, in accordance with the proportion of the different components. The identification of these aggregates should contain, as a minimum, an indication of the producer and place of production, the class to which they belong and the size (particle size).

The materials produced with aggregates from C&DW whose composition is mostly concrete have been shown to have better properties (better mechanical strength, less water absorption, etc.) and are more uniform in their physical and chemical properties in comparison with materials produced using recycled aggregates composed mostly of masonry. This behaviour is related to the fact that concrete aggregate consists of a smaller number of materials (cement mortar and sand, crushed stone and additives for concrete) than masonry aggregate, so the latter are only used for concrete with few requirements.

Coarse recycled aggregates are used to manufacture concretes with hydraulic binders. Recycled aggregates cannot be used to manufacture concretes that will be in contact with drinking water. There are only two classes of recycled aggregates that can be used to manufacture concrete for use in regular or reinforced concrete elements. Nonetheless, in the case of reinforced concrete, the maximum amount of recycled aggregates for concrete is subject to limits.

For regular, filler or blinding concrete in nonaggressive environments, the amount to be included is not subject to any limits. The materials used for filler should be hard and have a narrow range of particle sizes, so that they are easily consolidated and keep their drainage performance. They should be chemically inert and have a stable volume in the presence of water. Masonry recycled material should not be used, since it may contain expansive material or wood, which after decomposing may leave voids in the filler.

The use of recycled aggregates from concrete in the manufacture of concretes with structural functions is also subject to some limitations, for example, in terms of the proportion amongst the aggregates used, so as to avoid possible variations in modulus of elasticity, creep, shrinkage and properties linked to durability.

In terms of chemical reactivity, recycled aggregates are considered to be potentially reactive. However, recent studies show that with the exception of recycled aggregates from floor blinding, recycled aggregates can be classified as nonreactive, even if they come from concretes manufactured using reactive aggregates.

No demands or rules were defined for the use of fine recycled aggregates, given that they generally contain a high proportion of elements with a particle size of less than 0.063 mm, which are damaging because of the greater adhering mortar content, their more angular shape and the fact that they have significant amounts of sulphates and other impurities, thereby requiring more water absorption to maintain workability and compromise the concrete's mechanical strength.

When good-quality material is desired for structural elements, only the coarse part of the recycled material from concrete should be used.

The elasticity modulus for concretes containing recycled material is generally lower than that for conventional concretes, even if the recycled material use is from concretes. This can be explained by the presence of mortar adhered to the recycled material, which has a lower modulus of elasticity and decreases the concrete's modulus. The specific mass of concretes containing recycled material is generally less than that of conventional concrete, due to the difference in mass of recycled aggregates. The tensile, flexion and shear strengths of concretes containing recycled material are also lower than those of conventional concretes, whilst creep, shrinkage and loss through abrasion have higher values.

Water absorption by concretes is linked to porosity and permeability. This is directly linked to the occurrence of carbonation. More porous concretes tend to have lower mechanical strength and are more susceptible to carbonation and chemical attacks. Because of their greater capacity for absorption, recycled material should be saturated before coming into contact with the binders to prepare the new product, because otherwise the aggregate may absorb part of the water needed for the cement to hydrate, damaging the quality of the material.

Shrinkage linked to the curing process for concrete produced using recycled inert material is higher than that of concrete produced using natural inert material because shrinkage values depend on the total surface area, and, in recycled inert material, the surface area is greater because of the presence of cement paste. Another aspect that may contribute to greater shrinkage for concrete produced using coarse recycled inert material is the greater deformability that this material has.

The durability of concrete made with recycled inert material is influenced by the factors mentioned, although the most significant is the presence of contaminants. The type of contaminant and the admissible content values depend on the type of use for the recycled material, being the amount of impurities greater for finer recycled aggregates.

One of the most damaging compounds in recycled aggregate is plaster, since sulphates may lead to the expansion of the new product. Chlorides may lead to steel corrosion, and some standards significantly limit their proportion in recycled material. Glass content should also be limited because alkali-silica reactions may take place when the new material is prepared and in contact with cement and with the presence of water.

Corrosion of the reinforcements in concrete made with recycled concrete takes place more quickly than in conventional concretes. The time that corrosion of steel bars begins is practically the same for concretes containing recycled material and conventional concretes, but if masonry waste is used, the time is slightly shorter. Once corrosion begins, the corrosion rate is the same regardless of the type of aggregate.

Using recycled aggregates in concrete is a promising alternative for civil construction, since natural inert material (sand and gravel) should be reserved for more prestigious uses, such as high-resistance concrete, and concrete without structural functions can be produced with recycled aggregates.

Another type of waste to be considered are the bituminous mixtures mentioned in [53], which come from the construction, rehabilitation, conservation and demolition of road and airport surfaces, known as C&DW. These mixtures may consist of milled bituminous mixtures, plates taken from pavement layers that are later disaggregated and/or crushed, or surplus materials from the production of bituminous materials. After recovery and after they have been kept separately according to origin, they should be stored carefully, protected from atmospheric actions, in order to prevent contamination and runoff.

The properties to be considered, when using recovered bituminous mixtures in the manufacture of recycled mixtures, are the material's maximum particle size, its nature (e.g. polluting components, namely, tar), shape, size and content, and the size of the aggregate contained in it, as well as the presence of extra matter, the characteristics of the recovered binder and the content of the binder. Further to these characteristics, the provenance of the materials should also be mentioned, in particular the works and type(s) of layer(s) from which they were extracted.

The rate for incorporating the recovered mixture depends on its characteristics and type of use, for example, if it is a wear layer or a blinding or base layer.

The tests carried out as quality control for the recycled mixture are similar to those performed for traditional bituminous mixtures.

Other types of recycled aggregates not included in [55] are those that come from construction, rehabilitation and demolition works for buildings, transport infrastructure or other civil engineering structures, also known as C&DW [57]. These aggregates may be formed of crushed concretes, aggregates from non-bound pavement layers, masonry and bituminous mixtures, and may be used as recycled aggregates in non-bound road surface layers (base and sub-base).

The recycled aggregates covered in this LNEC specification [57], for the purposes of use in non-bound road surface layers, are grouped into two classes, which depend on the waste's components, and three categories, which depend on its geometric and physical properties. The identification of these aggregates should contain, as a minimum, an indication of the producer and place of production, the class to which they belong and the size (particle size).

Recycled aggregates with larger particle sizes, when used in base and sub-base layer, may need to be mixed with natural aggregates, mostly with a view to correcting particle size.

The use of recycled materials from C&DW consisting of waste from construction, rehabilitation and demolition works for buildings, transport infrastructure or other civil engineering structures, is covered by LNEC specification E 474-2009 [58]. They may be used as materials for earthwork and bed layers for transport infrastructure, although they cannot be used in areas where they may come into contact with underground water or for drainage systems or in areas that flood frequently.

The alkaline level of this C&DW, concrete and masonry structures, is normally high, so they cannot be used in close proximity to materials susceptible to corrosion in that kind of environment, such as aluminium and galvanised piping.

The recycled materials covered by this specification are grouped into three classes, based on the relative proportions of each component, and two categories, based on geotechnical characteristics.

Just as for recycled materials established in the previous specifications, the identification of these recycled materials should contain at least an indication of the producer and place of production, the category to which they belong and the maximum particle size.

This type of recycled material, along with the recycled aggregates mentioned in [55, 57], should be stored separately, according to origin and main components, and can be used in combination with waste from different origins provided that they are mixed properly and under conditions that ensure homogeneity throughout the recycled material.

Conclusions

Sustainable development as a form of economic development, which uses natural resources and the environment in favour of today's society and future generations, is a real concern for the civil construction industry. These issues should modify the entire pattern of developing and assessing civil construction projects, making technicians responsible not only for the construction stage but also for the working life and demolition stages, minimising the consumption of non-renewable raw materials and water by using new construction technology and products.

The civil construction industry should try to close its production, material and energy cycle as far as possible in thermodynamic terms. The waste produced should, whenever possible, be reused and/or recycled, and any waste that is not recoverable should therefore be sent to landfills without posing a danger to the environment.

Recycling C&DW means reducing the quantity of materials disposed of in landfills, as well as less consumption of raw materials.

Recycling waste from other industries to produce materials for the civil construction industry should be investigated and is an important practice for sustainability.

Developing products that contain waste, some of which may be considered dangerous, is a multidisciplinary activity and needs to be done carefully and following criteria so as to ensure the success of these products on the market.

Introducing alternative products to the market for the same function and, possibly, more suitable solutions for specific situations, with increases in the general effectiveness of the process, will reduce production costs and may contribute to a reduction in the costs of housing and road and rail infrastructure, dams, etc.

The Waste Directive 2006/12/EC of the European Parliament and of the Council of 5 April 2006 establishes a goal for 2020 that 70 % of C&DW produced in member states must be sent for recycling. Although there are no official statistics, it is unanimous that Portugal is still far from reaching this amount.

Executive Law no. 73/2011, which alters the general regime for managing waste, transposes Directive 2008/98/EC of 19 November of the European Parliament and of the Council and considers that strengthening the prevention of waste production and encouraging its reuse and recycling is a priority, with a view to prolonging waste's use for the economy before returning it to the environment. Furthermore, it considers promoting the full use of the new organised waste market (OWM) to be important, as a way of strengthening waste recovery, with advantages for economic agents, as well as stimulating the use of specific waste with high recovery potential.

References

1. Habert G, Billard C, Rossi P, Chen C, Roussel N (2010) Cement production technology improvement compared to factor 4 objectives. Cement Concr Res 40(5):820–826
2. John VM, Zordan SE (2001) Research & development methodology for recycling residues as building materials—a proposal. Waste Manag 21(3):213–219
3. John VM (2000) Reciclagem de resíduos na construção civil: contribuição à metodologia de pesquisa e desenvolvimento. Livre docência thesis. Escola Politécnica da Universidade de São Paulo, São Paulo, Brazil
4. Matos C, Wagner L (1999) Consumption of materials in the United States, 1900-1995. US Geological Survey, Reston
5. Commission of the European Communities (2005) Strategy on the sustainable use of natural resources. Commission of the European Communities, Brussels
6. Construire un monde durable (2008) Les élements et mineraux. Les 12 métaux les plus exploités. Science & Vie. Hors-série no 243. ISSN: 01510282
7. Mália MAB (2010) Indicadores de resíduos de construção e demolição. Master's dissertation in Civil Engineering. IST/UTL, Lisbon, Portugal
8. Canha da Piedade A (2000) Construir no presente, preservando o futuro. Ingenium. Lisbon, Portugal
9. Bernstein HM (1996) Bridging the globe: creating an international climate and challenges of sustainable design and construction. Ind Environ 29(2):26–28
10. Pérez-Lombard L, Ortiz J, Pout C (2008) A review on buildings energy consumption. Energ Build 40(3):394–398
11. Conroy A, Halliwell S, Reynolds T (2006) Composite recycling in the construction industry. Compos Part A Appl Sci Manuf 37(8):1216–1222
12. Péra J, Ambroise J, Chabannet M (2004) Valorization of automotive shredder residue in building materials. Cement Concr Res 34(4):557–562
13. Cheriaf M, Rocha JC, Péra J (1999) Pozzolanic properties of coal combustion bottom ash. Cement Concr Res 29(9):1387–1391
14. Amorim LV, Pereira ASG, Neves GA, Ferreira HC (2000) Reciclagem de rejeitos de cerâmica vermelha e da construção civil para obtenção de aglomerantes alternativos. Cerâm Ind 5 (4):35–46
15. Tam VWY, Tam CM (2006) A review on the viable technology for construction waste recycling. Resour Conservat Recycl 47(3):209–221
16. Gonçalves APF (2001) Análise do desempenho de betões produzidos a partir de inertes reciclados provenientes de resíduos da construção. Master's dissertation in Civil Engineering. IST/UTL, Lisbon, Portugal
17. Oliveira JFS (2005) Gestão Ambiental. Lidel, Lisbon
18. Life cycle thinking and assessment. European Commission-Joint Research Centre. Institute for the environment and sustainability. http://lct.jrc.ec.europa.eu/assessment. Accessed 2 Nov 2011
19. Azapagic A (1999) Life cycle assessment and its application to process selection, design and optimization. Chem Eng J 73(1):1–21
20. ISO 14040:2006 (2006) Environmental management-life cycle assessment-principles and framework. International Organisation for Standardization (ISO), Geneva
21. ISO 14044:2006 (2006) Environmental management-life cycle assessment-requirements and guidelines. International Organisation for Standardization (ISO), Geneva
22. Curran MA (1996) Environmental life-cycle assessment. McGraw-Hill, New York

23. Corbitt RA (1990) Standard handbook of environmental engineering. McGraw-Hill, New York
24. SimaPro Analyst (2011) Pre consultants, Holland
25. Chaves RS (2009) Avaliação da implementação do Plano de Prevenção e Gestão de Resíduos de Construção e Demolição. Master's dissertation in Environment Systems Management. FCT/UNL, Lisbon, Portugal
26. Instituto dos Resíduos (2001) Plano Nacional de Prevenção de Resíduos Industriais (PNAPRI). Lisbon, Portugal
27. Waste & Recycling. Waste hierarchy. www.environmental-register.co.uk. Accessed 3 Oct 2011
28. Commission of the European Communities (2005) Taking sustainable use of resources forward: a thematic strategy on the prevention and recycling of waste. Commission of the European Communities, Brussels
29. Our Common Future (1991) Report by the World Committee on Environment and Development (WCED). Meribérica/Liber Editores Lda, Lisbon
30. Ferrão P (1998) Introdução à gestão ambiental: a avaliação do ciclo de vida de produtos. IST Press, Lisbon
31. Bossink BAG, Browers HJH (1996) Construction waste: quantification and source evaluation. J Constr Eng Manage 122(1):55–60
32. Hillier SR, Sangha CM, Plunkett BA, Walden PJ (1999) Long-term leaching of toxic trace metals from Portland cement concrete. Cement Concr Res 29(4):515–521
33. Aidonis D, Xanthopoulos A, Vlachos D, Iakovou E (2008) An analytical methodological framework for managing reverse supply chains in the construction industry. WSEAS Trans Environ Dev 4(11):1036–1046
34. Pereira LC (2002) Reciclagem de resíduos de construção e demolição: aplicação à zona norte de Portugal. Master's dissertation in Civil Engineering. University of Minho, Guimarães, Portugal
35. Clark C, Jambeck J, Townsend T (2006) A review of construction and demolition debris regulations in the United States. Crit Rev Environ Sci Tech 36:141–186
36. Tokyo Metropolitan Government (2006) Environmental white paper 2006. http://www2.kankyo.metro.tokyo.jp/kouhou/env/eng/environment08.html. Accessed 29 Apr 2014
37. Kloek W, Blumenthal K (2009) Environment and energy, generation and treatment of waste. EUROSTAT. http://ec.europa.eu/eurostat/. Accessed 2 Nov 2011
38. Resíduos de Construção e Demolição (2004) MAOTDR/IGAOT, Portugal
39. Ekanayake L, Ofori G (2000) Construction material waste source evaluation. In: Proceedings of the conference "strategies for a sustainable built environment", Pretoria, South Africa, pp. 35-1–35-6
40. Nixon PJ (1976) The use of materials from demolition in construction. J Resour Pol 2(4):276–283
41. Lima JAR (1999) Proposição de directrizes para produção e normalização de resíduos de construção reciclado e de suas aplicações em argamassas e concretos. Master's dissertation in Architecture and Urban Planning, University of São Paulo, São Paulo, Brazil
42. Materials characterization paper in support of the final rulemaking: identification of nonhazardous secondary materials that are solid waste-construction and demolition materials-building related C&D materials (2011) Document ID: EPA-HQ-RCRA-2008-0329-1811, (EPA), USA
43. Rao A, Jha KN, Misra S (2007) Use of aggregates from recycled construction and demolition waste in concrete. Resour Conservat Recycl 50(1):71–81
44. Symonds Group (1999) Construction and demolition waste management practices, and their economic impacts. DGXI report, European Commission. www.ec.europa.eu. Accessed 2 Nov 2011
45. Commission of the European Communities (2003) For a thematic strategy on the prevention and recycling of waste. Commission of the European Communities, Brussels

46. Agência Portuguesa do Ambiente (2011) http://www.apambiente.pt. Accessed 2 Nov 2011
47. Coelho A, Brito J (2010) Análise da viabilidade de implantação de centrais de reciclagem de resíduos de construção e demolição em Portugal: Parte I-Estimativa da geração de resíduos de construção e demolição. ICIST Report. DTC no. 04/2010. IST/UTL, Lisbon
48. Tchobanoglous G, Kreith F (2002) Handbook of solid waste management, 2nd edn. McGraw-Hill, New York
49. European Commission (2000) The ETN recycling in construction. Use of recycled materials as aggregates in the construction industry. European Commission, Brussels
50. Carvalho PLG (2001) Gestão de resíduos na construção. Master's dissertation in Construction. IST/UTL, Lisbon, Portugal
51. John VM (1995) Cimentos de escória ativada com silicatos de sódio. Doctoral thesis in Engineering, University of São Paulo, Brazil
52. European Environmental Agency (EEA) (2003). Environmental assessment. www.eea.europa.eu/publications/environmental_assessment_report_2003_10. Accessed 2 Nov 2011
53. Tomas J, et al (1999) Liberation and separation of valuables from building material waste. In: Proceedings from the conference "global symposium on recycling, waste treatment and clean technology", San Sebastian, Spain
54. Gonçalves AP (2001) Análise do desempenho de betões obtidos a partir de inertes reciclados provenientes de resíduos da construção. Master's dissertation in Civil Engineering, IST/UTL, Lisbon, Portugal
55. Guia para a utilização de agregados reciclados grossos em betões de ligantes hidráulicos. Especificação LNEC E 471-2009. Lisbon, Portugal
56. Guia para a reciclagem de misturas betuminosas a quente em central. Especificação LNEC E 472-2009. Lisbon, Portugal
57. Guia para a utilização de agregados reciclados em camadas não ligadas de pavimentos. Especificação LNEC E 473-2009. Lisbon, Portugal
58. Guia para a utilização de agregados reciclados em camadas não ligadas de pavimentos. Especificação LNEC E 474-2009. Lisbon, Portugal

LNEC Technical Approval and Construction Products Certification

19

Pedro Pontífice

Abstract

This chapter includes some topics about the new Construction Products Regulation (CPR) and the CE marking according to it, emphasising the main differences to the previous Construction Products Directive. Reference is made to the background, the general philosophy and the legal status of the CPR, along with some relevant details of the CPR.

A short summary of the history of LNEC Technical Approvals and its scope is made, and the steps involved in the development of a technical approval study are presented.

Finally, a brief reference to LNEC Application Documents is included, and considerations related to the certification of construction products and to the importance of the European technical harmonisation for all stakeholders in the construction industry are referred to.

Keywords

Regulation • CE Marking • CPR • CE • Technical approval

19.1 Foreword

The present chapter cannot be considered a translation of the chapter included in the Portuguese edition of this book, published by IST Press.

In fact, at the same time that the chapter was drafted, the Council Directive 89/106/EEC [1]—currently designated as Construction Products Directive (CPD)—was in the process of revision, and the publication of the Regulation of

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M.C. Gonçalves, F. Margarido (eds.), *Materials for Construction and Civil Engineering*, DOI 10.1007/978-3-319-08236-3_19

the European Parliament and the Council intended to repeal the CPD was foreseen; the Portuguese version of the book referred to this situation, and, besides information about the CPD and the CE marking of construction products according to this Directive, a very short notice was given about the Regulation.

The Regulation was published in April 2011—Regulation No. 305/2011 of the European Parliament and the Council, of 9 March 2011 [2]—and came into force on the 20th day following its publication, repealing the CPD; however, in order to assure a transition period where several actions had to be taken, the Regulation—usually named as Construction Products Regulation (CPR)—foresaw that its practical application was delayed to 1 July 2013.

Taking into account this situation, the present chapter has no longer references to the CPD as the Portuguese version had; it includes, in the next section, some topics about the new CPR and the CE marking according to it, emphasising the main differences to the previous CPD.

19.2 Topics About the Construction Products Regulation and the CE Marking

19.2.1 Background

Following the Lisbon strategy adopted by the European Commission, a large initiative was launched in 2005 called “Better Regulation: Simplification Strategy” which included several actions. The revision of the CPD was one of those actions, and the objective of the European Commission was “to clarify and reduce the administrative burden of the CPD, and in particular for small and medium-sized enterprises (SMEs), through increased flexibility in the formulation and use of technical specifications, lighter certification rules, and the elimination of the implementation obstacles that so far have hampered the creation of a full internal market for construction products” [3].

Impact assessment studies were carried out, and a large consultation of the EU Member States was made; following the discussions between the European Commission, the European Council and the European Parliament, the *Regulation* (*EU*) *No. 305/2011 of the European Parliament and of the Council of 9 March 2011 laying down harmonised conditions for the marketing of construction products and repealing the Council Directive 89/106/EEC* was published in the Official Journal of the European Union (OJEU) [2].

According to the European Commission, the CPR provides more clarification of the concepts and the use of CE marking and introduces simplified procedures, which will reduce the costs incurred by enterprises, in particular small and medium enterprises (SMEs) [4].

In [4], the European Commission also states that the aim of the CPR is to ensure reliable information on construction products in relation to their performances providing a “common technical language”, by establishing uniform assessment methods of the performance of construction products—throughout harmonised

European standards (hEN) and European Assessment Documents (EAD)—which shall be used by:

- Manufacturers when declaring the performance of their products
- Authorities of Member States when specifying requirements for them
- Users (architects, engineers, constructors, etc.) when choosing the products most suitable for their intended use in construction works

It is clearly out of the scope of this chapter to go into details about CPR, and there is nowadays a large amount of information available about the Regulation, namely, in [4], where recently a list of FAQs has been added. In spite of that, in the next section of this chapter some aspects are referred to, particularly those representing a change facing the "old" CPD. However, before that comparison, three aspects shall be emphasised.

Firstly, it should be noticed that the CPR is just one piece of a larger horizontal framework recently published concerning the marketing of products in the European Union, involving two regulations and one decision of the European Parliament and the Council published in 2008 [5–7]. This legislation will be the basis for the revision of several European Directives that will be undertaken soon.

Secondly, it should be said that CPR is, by a great extent, in line with the philosophy established in the previous CPD. However, some changes were introduced, and a lot of work is presently ongoing in order to clarify some aspects concerning the practical implementation of CPR.

Finally, the CPR foresees that, with the purpose of achieving its objectives, in particular removing and avoiding restrictions on making construction products available on the market, the European Commission can issue, by delegated acts and for some specific aspects established in the CPR itself, legislation amending or complementing the CPR. Using this prerogative, legislation as already been published in the OJEU concerning the format of the European Technical Assessment (ETA) for construction products [8], the conditions for making available on a website a copy of the declaration of performance issued by the manufacturers [9], and the amendment of Annexes III and V of the CPR [10, 11].

19.2.2 Construction Products Regulation (CPR) Versus Construction Products Directive (CPD)

(a) Legal Status

One of the main differences between the CPR and the CPD is directly related to the legal status of the documents; in fact, a directive implies the respective implementation in each Member State—in Portugal, a Decree-Law has been published with this objective—and a regulation is entirely and directly applicable to the Member States, and no implementation is needed.

This difference is really of major importance in relation to the degree of harmonisation achieved as it is known that the implementation of the former CPD was not done in the same way. To illustrate this situation, it should be noticed that, in the majority of the EU Member States, the CE marking under the CPD was considered mandatory, but in four of them, this was not the case.

(b) Table of Contents, Definitions and Terminology

The CPD had 24 articles and four annexes, and the CPR has 68 articles, five annexes and 58 recitals. With these figures, a more complexity of the CPR could be presumed; in fact, this is not really the case, as the Regulation includes a certain number of procedures which has been implemented during the period of validity of the Directive, but only now are explicitly foreseen in the text of the document.

The chapters and the annexes of the Regulation are the following:

Chapter I—General provisions
Chapter II—Declaration of performance and CE marking
Chapter III—Obligations of economic operators
Chapter IV—Harmonised technical specifications
Chapter V—Technical Assessment Bodies (TAB)
Chapter VI—Simplified procedures
Chapter VII—Notifying authorities and notified bodies
Chapter VIII—Market surveillance and safeguard procedures
Chapter IX—Final provisions
Annex I—Basic requirements for construction works
Annex II—Procedure for adopting a European Assessment Document (EAD)
Annex III—Declaration of performance
Annex IV—Product areas and requirements for TABs
Annex V—Assessment and verification of constancy of performance

The Regulation includes, in article 2, a list of definitions, which was clearly missing in the Directive. The meaning of "construction product" and "construction works" is basically the same in both documents.

However, the CPR adopts a different terminology to express basically the same concepts of the CPD. In Table 19.1, some of those differences are highlighted.

(c) General Philosophy

The scope of the Regulation established in article 1 is clear; the Regulation "lays down conditions for the placing or making available on the market of construction products by establishing harmonised rules on how to express the performance of construction products in relation to their essential characteristics and on the use of CE marking on those products".

Furthermore, a key role is given to the declaration of performance issued by the manufacturer. In fact, in articles 4 and 6 of the Regulation, it is established that, when a construction product is covered by a harmonised European standard or conforms to a ETA that has been issued for it, the manufacturer shall

Table 19.1 CPR versus CPD: differences in terminology

Subject	CPR	CPD
Requirements of construction works	Basic requirements for construction works (seven requirements)	Essential requirements for construction works (six requirements)
Characteristics of construction products	Essential characteristics	Harmonised characteristics
		Essential characteristics
Harmonised technical specifications	Harmonised European standard	Harmonised European standard
	European Assessment Document (EAD)	European Technical Approval (ETA)
Assessment systems for CE marking	Assessment and verification of constancy of performance systems	Attestation of conformity systems
	1+, 1, 2+, 3, 4	1+, 1, 2+, 2, 3, 4
Declaration of the manufacturer	Declaration of performance	Declaration of conformity
European Technical Approval/Assessment	European Technical Assessment (ETA)	European Technical Approval (ETA)
Technical guidelines for issuing ETA	Guidelines for European Technical Approvals (ETAG)	European Assessment Document (EAD)
	Common Understanding for Assessment Procedure (CUAP)	

draw up a declaration of performance when such a product is placed on the market; in this case, the manufacturer shall assume responsibility for the conformity of the construction product with such declared performance, and Member States shall presume the declaration of performance drawn up by the manufacturer to be accurate and reliable, in the absence of objective indications to the contrary.

Article 8 of the Regulation sets finally that CE marking shall be affixed to those construction products for which the manufacturer has drawn up a declaration of performance, and by affixing or having affixed the CE marking, the manufacturers indicate that they take responsibility for the conformity of the construction product with the declared performance, as well as the compliance with all applicable requirements laid down in the Regulation and in other relevant Union harmonisation legislation providing for its affixing.

It should be noticed that, according to the Regulation, CE marking is mandatory for a construction product covered by a harmonised European standard or conforming to a ETA that has been issued for it; this was not the case during the life of the Directive, where four Member States never imposed this status.

On the other hand, expressions of the Directive linking the CE marking with the assumption of the fitness for use of a construction product are no longer included in the Regulation. In fact, the CE marking means that manufacturers take responsibility for the conformity of the construction product with the declared performance; it is up to the users (architects, engineers, constructors, etc.) to evaluate if the declared performance is suitable for the construction works where the construction product is going to be incorporated.

(d) Basic Requirements for Construction Works

The CPR establishes, in Annex I, 7 basic requirements for construction works, in line with the essential requirements set in the CPD. Basic requirement no. 1 (mechanical resistance and stability), no. 2 (safety in case of fire) and no. 5 (protection against noise) are expressed in an identical way of the CPD; concerning Basic requirement no. 6 (energy economy and heat retention), a reference to the energy used during the construction and dismantling of construction works has been added; the scope of Basic requirement no. 3 (hygiene, health and the environment) was significantly enlarged, and the scope of Basic requirement no. 4 (safety and accessibility in use) has also been expanded, and aspects related to accessibility and use for disabled persons shall now be taken in consideration; finally, a new Basic Requirement no. 7 (sustainable use of natural resources) was added establishing that "construction works must be designed, built and demolished in such a way that the use of natural resources is sustainable and in particular ensure the following: (a) reuse or recyclability of the construction works, their materials and parts after demolition; (b) durability of the construction works; (c) use of environmentally compatible raw and secondary materials in the construction works".

It should be noticed that these changes will be progressively put in force; in fact, it is now necessary, namely, to revise the harmonised European standards in order to take into account the new basic requirements, establishing the essential characteristic of the products that are related to the those new basic requirements of the construction works. This is a hard task, and it will take some time to adjust all the technical specifications already published.

(e) European Technical Assessment (ETA)

Under the CPR, the activity concerning the CE marking of innovative construction products (basically, products not covered or not fully covered by any harmonised European standard) presents some changes in relation to the procedures set in the CPD. One slight modification but with significance is the change from European Technical Approval (under CPD) to ETA (under CPR).

In fact, the Regulation follows the opinion of the European Commission which assumes that the new ETA (ETAssessment) is significantly different from the old ETA (ETApproval) as the first one cannot be considered an approval to place the product on the market but it is only a documented assessment of the performance of a construction product, in relation to its essential characteristics for the foreseen intended use.

It also becomes clear in the Regulation (as it was assumed under the Directive) that a manufacturer producing a construction product not covered or not fully covered by any harmonised European standard is not obliged to ask for an ETA for its product, and, consequently, it will not have CE marking.

In order to issue an ETA, a EAD needs to be prepared following the detailed rules established in Annex II of the CPR, under a close supervision of the members of the European Organisation for Technical Assessment (EOTA) and of the European Commission. During a transitional period, Guidelines for European Technical Approvals (ETAG) published under the CPD can be used as EAD.

Finally, the bodies involved in this activity need to be designated by the Member States for specific areas and to fulfil a certain number of requirements, as stated in Annex IV of the CPR.

(f) Systems of Assessment and Verification of Constancy of Performance

The procedures established in Annex V of the CPR for the systems of assessment and verification of constancy of performance (briefly, AVCP systems) do not differ significantly of those established previously in the CPD.

Besides the difference in the terminology adopted (assessment and verification of constancy of performance in the CPR versus attestation of conformity in the CPD), the major differences can be summarised as follows:

- The number of systems has been reduced to five: 1+, 1, 2+, 3 and 4; system 2 foreseen in the CPD was eliminated.
- The inspection body foreseen at the CPD as a notified body was eliminated. So, notified bodies under the CPR are product certification body (for AVCP systems 1+ and 1), factory production control certification body (for AVCP system 2+) and laboratory (for AVCP system 3).
- It is possible to make a "horizontal" notification, where bodies are not notified by reference to a harmonised technical specification, but the notification is made for certain essential characteristics of the products: reaction to fire, resistance to fire, external fire performance, acoustic performance and emissions of dangerous substances.
- Under AVPC system, 1+ audit-testing of samples taken on the market and on the construction site, as foreseen in the CPD, is no longer possible and is limited to samples taken before placing the product on the market.

In Table 19.2 the different tasks involved in the five AVCP systems are summarised. It should be noticed that, similarly to the situation under the CPD, in system 4, the responsibility of all tasks to be carried out is exclusively of the manufacturer, and in all the systems, the manufacturer shall carry out a factory production control.

Finally, it should be referred to that the CPR includes an entire chapter establishing the procedures applicable to the notifying authorities and notified bodies (Chapter VII, with 16 articles); in Portugal, the responsibility for the notification to the European Commission is assigned to the Portuguese Institute

Table 19.2 Systems of assessment and verification of constancy of performance

System	Tasks of the manufacturer	Task of the notified body	Basis for the CE marking
1+	(i) Factory production control	Product certification on the basis of:	Declaration of performance of the product by the manufacturer on the basis of a certificate of constancy of performance issued by the notified body
	(ii) Testing of samples in accordance with the prescribed test plan	(a) Assessment of the performance of the product carried out on the basis of testing, calculation, tabulated values or descriptive documentation of the product	
		(b) Initial inspection of the manufacturing plant and of factory production control	
		(c) Continuous surveillance, assessment and evaluation of factory production control	
		(d) Audit-testing of samples taken before placing the product on the market	
1	(i) Factory production control	Product certification on the basis of:	
	(ii) Testing of samples in accordance with the prescribed test plan	(a) Assessment of the performance of the product carried out on the basis of testing, calculation, tabulated values or descriptive documentation of the product	
		(b) Initial inspection of the manufacturing plant and of factory production control	
		(c) Continuous surveillance, assessment and evaluation of factory production control	

(continued)

Table 19.2 (continued)

System	Tasks of the manufacturer	Task of the notified body	Basis for the CE marking
2+	(i) Assessment of the performance of the product carried out on the basis of testing, calculation, tabulated values or descriptive documentation of the product	Factory production control certification on the basis of:	Declaration of performance of the product by the manufacturer on the basis of a certificate of conformity of the factory production control issued by the notified body
	(ii) Factory production control	(a) Initial inspection of the manufacturing plant and of factory production control	
	(iii) Testing of samples in accordance with the prescribed test plan	(b) Continuous surveillance, assessment and evaluation of factory production control	
3	Factory production control	Assessment of the performance of the product carried out on the basis of testing, calculation, tabulated values or descriptive documentation of the product	Declaration of performance of the product by the manufacturer
4	(i) Assessment of the performance of the product carried out on the basis of testing, calculation, tabulated values or descriptive documentation of the product	No tasks	
	(ii) Factory production control		

Note: The information given in this table is taken from Annex V of the CPR

for Quality (*Instituto Português da Qualidade*—IPQ). Similarly to what has been done under the CPD, the European Commission established a database (NANDO) with all the notified bodies authorised by the Member States and all the Technical Assessment Bodies (TAB) responsible for issuing ETA designated by the Member States; the database NANDO for construction products can be found in the following URL: http://ec.europa.eu/enterprise/newapproach/nando/index.cfm?fuseaction=directive.notifiedbody&dir_id=33

(g) Example of a Label for the CE Marking

In Fig. 19.1, a schematic example of a label for the CE marking of a construction product, adapted to the rules established in the CPR, is presented. For each

CE	Logo of the CE marking, according to Regulation (EC) No. 765/2008
0123	Identification number of the notified body (if applicable)
AnyCo Ltd, PO Box 21, B-1050, Brussels, Belgium	Name and the registered address of the manufacturer, or identifying mark
14	Last two digits of the year in which the marking was first affixed
XXXX-CPR-2014/04/01	Reference number of the declaration of performance
EN 123-5:2009	Harmonised European standard applicable, as referenced in the OJEU
Product A	Unique identification code of the product type
Intended to be used in (e.g. curtain wall, fire compartmentation)	Intended use of the product as laid down in the harmonised European standard
Technical information about the essential characteristics	Essential characteristics listed in Annex ZA of the harmonised European standard

Fig. 19.1 Schematic representation of a label for the CE marking (adapted from [12])

product family, the consultation of the corresponding harmonised technical specification is needed, which includes detailed rules for this labelling.

It should be noticed that, for some of the essential characteristics of the product, a manufacturer can declare No Performance Determined (NPD) if those characteristics are not required at all (or are not required for a specific use) in the Member State where the manufacturer wishes to place the product on the market.

(h) Miscellaneous

Finally, some particular aspects of the CPR are highlighted:

- The CPR foresees the possibility of derogations from drawing up a declaration of performance when placing on the market a construction product covered by a harmonised standard (article 5); however, some clarification by the European Commission is needed concerning products manufactured in a non-series process and in response to a specific order.
- The CPR foresees simplified procedures that can be used by manufacturers in order to draw up a declaration of performance and to affix the CE marking to their construction products, namely, if they are classified as micro-enterprises, and by using appropriate technical documentation or specific Technical Documentation (Chapter VI); some clarification is also needed for some of these possibilities.

- The CPR allows that a copy of the declaration of performance is made available on a website, in accordance with certain conditions (see article 7 and [9]).
- The CPR defines the economic operators (manufacturer, distributor, importer and authorised representative) and establishes the respective obligations (Chapter III).
- The CPR establishes that Member States shall designate Product Contact Points for Construction in order to provide information on the provisions within their territories aimed at fulfilling the basic requirements for construction works applicable for the intended use of each construction product (article 10).

19.3 LNEC Technical Approvals

19.3.1 A History with Around 50 Years

The establishment of rules to assess the quality of innovative construction products and systems goes back to 1951, with the publication of the *Regulamento Geral das Edificações Urbanas* [13] (General Building Regulation), which in article 17, recently amended, stated that the application of new materials and construction processes for which there were no official specifications nor enough experience of use should be subjected to a previous evaluation by the National Laboratory of Civil Engineering (*Laboratório Nacional de Engenharia Civil*—LNEC).

While the issuing of assessments for innovative products and systems has then started, it was only from 1963 onwards that those technical assessments originated the issuing of LNEC Technical Approvals (*Documentos de Homologação*—DH), with four DH issued in that year, the first one referring to special steel reinforcement for concrete and the remaining three to precast concrete beam-and-block systems for floors.

A decisive factor for this evolution was the creation, in 1960, of the European Union of Agrément/Union Européenne pour l'Agrément Technique dans la Construction (UEAtc)—of which LNEC was co-founder together with other bodies with similar profile from Belgium, France, Spain, the Netherlands and Italy—that brought together the national bodies in charge of the technical approval of innovative products and building processes. The initial membership was meanwhile expanded, and the UEAtc includes presently 17 technical approval bodies from the same number of European countries.

During its 50 years of existence, UEAtc has mainly developed two complementary activities: on the one hand, the drafting of common approval guidelines and nowadays guides and technical reports—with the objective of laying down common criteria for the technical assessment of several families of innovative construction products—and, on the other hand, the creation and development of the procedure of confirmation of Technical Approvals—with the aim to make easier the issuing of a Technical Approval for imported construction products for which a

Technical Approval has been issued in the European country where they were manufactured. Meanwhile, due to the recent evolution in the field of technical harmonisation of innovative construction products in Europe, UEAtc has been losing some of its ground.

The role of LNEC in the UEAtc had several implications on the activity of several LNEC departments, mainly due to the need to create an experimental infrastructure allowing the execution of tests in order to assess these innovative products and systems. For the construction market, the most visible output of this activity is the publication of more than 900 LNEC Technical Approvals (DH) between 1963 and 2013.

However, the number of valid DH has come to decrease significantly over the last few years, as a result of the new legal framework for LNEC Technical Approvals. In order to prove this tendency, it is enough to compare the number of valid DH: at the end of 2013 was 27 and at the end of 2005 was 189; the reasons for this reduction will be discussed with more detail in Sect. 19.3.3.

19.3.2 Development of a Technical Approval Study

The issuing of a Technical Approval for an innovative construction product or system means that an independent entity (in this case the LNEC) has assessed the manufacturing conditions, the factory production control and the installation in the construction works and considers that the performance characteristics of the product or system, validated by testing, are fit for the intended use, defined in the Technical Approval.

The studies for these technical approvals are usually requested by the product and systems manufacturer, whether they are produced nationally or abroad. Following the request, LNEC prepares a work plan for the study and defines the respective cost and deadline. Basically, a technical approval study includes the following steps:

- Analysis of the technical documentation supplied by the manufacturer
- Assessment of the manufacturing process and factory production control, the installation in the works and the durability, namely, through visits to the manufacturing plant and to construction works in progress and in use
- Tests to assess the performance characteristics, carried out in test specimens taken by LNEC during the visit to the manufacturing plant
- Drafting and issuing of the LNEC Technical Approval (*Documento de Homologação*—DH), if the global assessment of all the previous actions is positive

A Technical Approval of a construction product or system issued by LNEC usually includes a general description of the product or system, the performance characteristics and the intended use, a global assessment, rules for storage, transportation and installation as well as the characteristics and respective tolerances to be evaluated within the scope of eventual reception tests. The Technical Approval has normally a period of validity of 3 years and can be renewed, whenever the manufacturer shows interest and LNEC gives a positive review, including, if necessary, the execution of new tests and re-evaluation of manufacturing and installation conditions, as well as of the fitness for use.

Along with the issuing of ordinary Technical Approvals, LNEC started, some years ago, to issue Technical Approvals with Certification. In this type of Technical Approval, the manufacturing is subjected to a factory production control by the manufacturer, and LNEC (or an external body recognised as competent by LNEC) performs periodic audits to the factory for evaluating the maintenance of the manufacturing conditions and the factory production control and collecting samples to be tested at LNEC. Technical Approvals with Certification have, at present, a period of validity of 5 years as long as, during this period, the production conditions are maintained, and the test results are satisfactory.

Concerning imported construction products or systems covered by a Technical Approval issued by the member of UEAtc of the country of origin, LNEC will perform a confirmation study developed according to UEAtc rules that, if concluded with positive results, will give rise to a LNEC Technical Approval. Such study includes basically the verification that the construction procedures for the incorporation in the works established in the original approval (possibly complemented with additional requirements expressed in Portuguese regulations) are being respected and normally also includes the performing of identification tests on samples collected from the authorised manufacturer's representative in Portugal, in order to ensure that the product being imported actually matches the one that is covered by the original Technical Approval. In this case, the period of validity of the LNEC Technical Approval is usually linked with the validity of the original Technical Approval, expiring when the original approval does.

19.3.3 Scope of LNEC Technical Approval

In the meantime, the activity concerning the technical approval of construction products developed by LNEC over 50 years is nowadays affected by a new legal framework, as a result of the efforts of technical harmonisation regarding construction products carried out at the European Union. The strongest evidence of this harmonisation was the publication, in 1998, of the Council Directive 89/106/EEC [1], followed recently by the publication of the Regulation (EU) No. 305/2011 of the European Parliament and of the Council of 9 March 2011 [2], which repealed that directive. As referred to previously, this Regulation lays down harmonised conditions for the marketing of construction products within the EU and established a mandatory status for the CE marking of a construction product placed in the market, if the product is covered by a harmonised European standard or conforms to a ETA that has been issued for it.

As a result of this situation, the set of standards published or adopted in Portugal regarding construction products, which was very small a decade ago, increased very significantly. This situation led LNEC to stop issuing Technical Approvals for products covered by those standards because this approval was, since its creation, devoted to innovative products not covered by official specifications, namely, standards.

As a result of this new reality, the legal framework for LNEC Technical Approvals has changed in Portugal by the publication of the Decree-Law no. 50/2008, of 19 March [14], that redrafted article 17 of the General Building Regulation [13], within the scope of which LNEC had issued Technical Approvals for almost 50 years.

According to this Decree-Law, construction products and systems installed in construction works built in urban areas—and as far as they have an effect on the performance of works with respect to the basic requirements defined in the Decree-Law—shall be covered by an LNEC Technical Approval, as long as:

- They are not covered by Portuguese standards or European standards adopted in Portugal.
- They are not covered by an ETA that has been issued for it.
- They are not subjected to mandatory certification, as it is presently the case for reinforcing steel for concrete (Decree-Law no. 390/2007 [15]) and for prestressing steel (Decree-Law no. 28/2007 [16]).

And since the conditions for the mutual recognition procedure established in article 5 of the Decree-Law are not met.

19.4 LNEC Application Documents

As a result of the new legal framework concerning LNEC Technical Approvals previously mentioned, the number of approvals issued by LNEC has decreased significantly in the last few years. In fact, for family products that are covered by a harmonised European standard where the CE marking is already possible, LNEC has ceased the issuing of Technical Approvals since the final date of the coexistence period defined in the OJEU, and the Technical Approvals issued previously to such date remain valid until the end of the period of validity, but they will not be renewed. Facing this situation, LNEC decided to start issuing a new type of technical assessment document for construction products, called Application Document (*Documento de Aplicação*—DA), similarly to what happened in other European countries.

This decision was mainly a direct result of the meaning of CE marking; in fact, this marking was designed to be a passport allowing the free circulation of the construction products in the European Economic Area, differing from a voluntary marking, whose main goal is the increase of value and the differentiation of the products in the market.

The Application Documents include aspects that are not covered by the harmonised technical specifications used for the CE marking of products, like the definition of the application field and possible use limitations, the performance characteristics, the evaluation of characteristics not covered by such marking considered to be relevant as well, the characteristics (and respective tolerances) to be evaluated within the scope of possible reception tests, the conditions for its installation in the construction works, rules for the proper maintenance and considerations about possible national particularities. It should also be noticed that Application Documents are issued on a voluntary basis, unlike the mandatory status of the Technical Approvals in several situations. Whenever the CE marking for a certain family of construction products is already mandatory, Application Documents for one of those products are only issued if such products bear the CE marking.

Recently, LNEC decided to enlarge the scope of the Application Documents to construction products covered by Portuguese standards, as well as non-harmonised European standards, which cannot be CE marked, according to Regulation (EU) No. 305/2011. Then, the scope of these two technical assessment documents issued by LNEC is the following: the Application Documents (*Documento de Aplicação*—DA) are issued for products covered by a European standard (harmonised, thus leading to the CE marking, or non-harmonised), by an ETA, by a Portuguese standard or by other official specification; the Technical Approvals (*Documento de Homologação*—DH) are issued for innovative products, in other words, products not covered by a Portuguese or European standard or deviating significantly from such standards. Similarly to what occurs with the Technical Approvals, Application Documents can also be issued with certification.

It is also important to emphasise that the decision to issue Application Documents in Portugal follows the policy adopted in many European countries. As a matter of fact, some of the bodies responsible for issuing national Technical Approvals are presently issuing this type of document. Additionally, several European countries with renowned voluntary certification schemes for construction products, recognised for a long time by stakeholders of the construction industry, have kept and even strengthened their voluntary quality marks, complementing the CE marking.

LNEC believes that issuing these Application Documents for construction products where LNEC has a solid expertise is a major contribution in order to ensure that products covered by standards, ETA or other official technical specification show an adequate performance when installed in the construction works, offering therefore additional warranties to the stakeholders of the construction activity.

Table 19.3 Different ways for the technical assessment of construction products by LNEC

Products	Yes	No
Covered by standards (EN, NP EN or NP) or by mandatory certification	DA (voluntary)	DH
Not covered by standards nor by mandatory certification (innovative products)	DH[a] or ETA (+possible DA)	

DA LNEC Application Document, *DH* LNEC Technical Approval, *EN* European standard, *NP EN* Portuguese translation of a European standard, *NP* Portuguese standard

[a] If the product does not bear the CE marking on the basis of an ETA and is to be installed in construction works built in urban areas, the DH is mandatory

In Table 19.3, the different ways for the technical assessment of construction products by LNEC are shown. The information in this figure does not contemplate the possibility of using the mutual recognition procedure, established in [5], which have to be analysed case by base.

19.5 The Certification of Construction Products

The concept of certification versus technical approval applied to construction products can give rise to confusion in some of the actors of the construction industry; the confusion increases when one of the formats that LNEC Technical Approvals can assume is precisely Technical Approvals with Certification.

Certification is, by definition, a procedure by which a third-party body independent from the manufacturer issues a written warranty attesting that a certain product, process or service meets specific requirements; this warranty is usually expressed by the issuing of a certificate by the third party stating that a product, process or service meets an applicable technical specification.

The product certification usually presumes an audit to the manufacturing conditions and to the factory production control implemented by the manufacturer, as well testing of samples taken at the factory by the certification body or by another body recognised by the certification body as competent to perform those tasks. It is important to point out the significant difference between this certification and the certification of the quality systems (e.g. according to EN ISO 9001 [17]); as a matter of fact, the quality system certification values mainly the way a company organises its resources in order to develop an activity, while the product certification values the final result of such activity.

The applicable technical specification previously mentioned corresponds normally to a standard; however, this correspondence is not always true as, for example, happens with Technical Approvals with Certification issued by LNEC. As referred to previously, in these cases, LNEC (or a body recognised as competent by LNEC) performs an external production control, which includes periodical

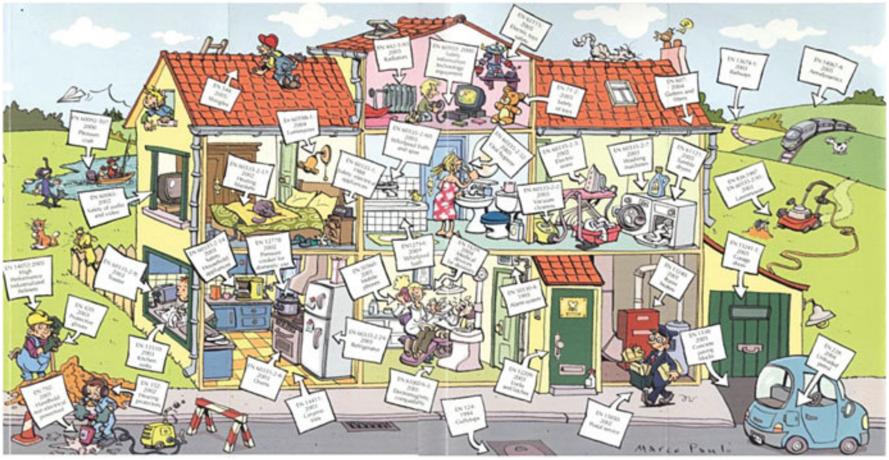


Fig. 19.2 Illustration of some products covered by harmonised European standards (partially reproduced from a leaflet published by CEN)

audits to the factory, with samples taken to be tested at LNEC, with the objective of verifying if the manufacturing conditions, the factory production control and the performance characteristics of the product, considered to be adequate at the date of issuing of the Technical Approval, are kept. In other words, LNEC (or another body) plays the role of the third party and states whether the product and its manufacturing fulfils the requirements established in the Technical Approval, which corresponds to the technical specification on which the certification is based.

Meanwhile, it is important to emphasise a relevant fact for all stakeholders in the construction industry, illustrated in Fig. 19.2; the figure intents to illustrate a small sample of the great diversity of products (not only construction products) that are covered by harmonised European standards and thus that shall bear the CE marking.

As referred to previously, the number of Portuguese standards concerning construction products was, some years ago, very small; in the last years, the situation deeply changed, and the number of European standards—which, even when not translated, are adopted in Portugal—is around 3,000 (including product standards and test standards), covering a large set of construction product families.

Therefore, it is vital that the stakeholders in the construction sector are aware of this new reality, in order to review and adapt their practices, in the design, in the specification of the construction works and in the building execution and its control. On the other hand, this big number of standards clearly facilitates the implementation of certification activities concerning construction products because those documents can be used as technical specifications for this certification.

In this chapter, reference has been often made to CE marking of construction products; it seems suitable to discuss one or two questions about this marking, recalling what has been said previously about this marking.

Among some of the actors of the construction industry, the expression "CE certification" is sometimes used as a synonym of CE marking. However, according to the information included in Table 19.2 concerning AVCP systems, it becomes clear that, for example, systems 3 and 4 (which apply to a significant number of construction product families) cannot be considered a product certification.

Additionally, it is important to be aware that, in the majority of the cases, the harmonised European standards do not establish any threshold level or class for the essential characteristics of the product declared by the manufacturer, even for those essential characteristics, the manufacturer may still use, whenever it is allowed to do so, the NPD option; finally, it should be remembered that the essential characteristics to be declared in the CE marking relate exclusively to those linked to the seven basic requirements for construction works, specified in Annex I of the CPR.

In conclusion, designers, contractors, construction owners and supervising bodies shall always analyse carefully if the declared essential characteristics of a product bearing the CE marking are suitable, taking into account the intended use of the product in the construction works.

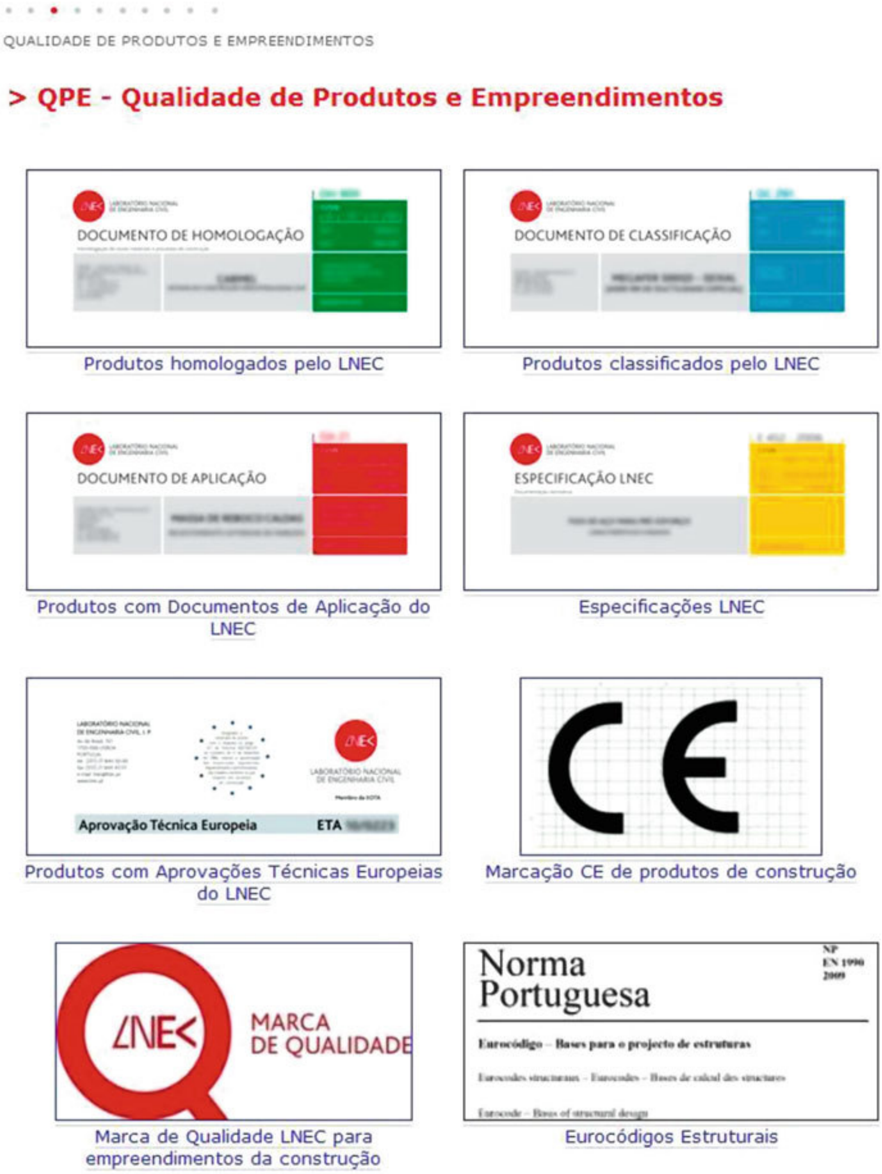
The situation described previously was one of the main reasons for starting issuing Application Documents by LNEC and by similar bodies in other European countries; it was also the reason why several European countries have kept and even strengthened their voluntary quality marks, complementing the CE marking.

In Portugal, the certification of construction products is expanding, but its importance is very far from the situation in other European countries; it is foreseeable that the certification will progress, and to make this happen, it is decisive that stakeholders of construction industry will adopt and strengthen a culture based on quality, crucial for the progress of every country.

19.6 Final Note

The major part of the information included in the present chapter can be found, in Portuguese, at LNEC website in the Internet (www.lnec.pt), opening the page *Qualidade de Produtos e Empreendimentos* (Quality of Products and Construction Works); Fig. 19.3 reproduces the front page of the URL www.lnec.pt/qpe.

The information given in those pages revelled to be very useful to the stakeholders; closely related to the theme of this chapter, it should be mentioned that, in the above URL, anyone can download, free of charge, the Technical Approvals, the Application Documents and the European Technical Approvals (under the CPD) issued by LNEC and in period of validity.



QUALIDADE DE PRODUTOS E EMPREENDIMENTOS

> QPE - Qualidade de Produtos e Empreendimentos

Produtos homologados pelo LNEC

Produtos classificados pelo LNEC

Produtos com Documentos de Aplicação do LNEC

Especificações LNEC

Produtos com Aprovações Técnicas Europeias do LNEC

Marcação CE de produtos de construção

Marca de Qualidade LNEC para empreendimentos da construção

Eurocódigos Estruturais

Fig. 19.3 Reproduction of the front page of the URL www.lnec.pt/qpe

References

1. Council Directive of 21 December 1988 on the approximation of laws, regulations and administrative provisions of the Member States relating to construction products (Directive 89/106/EEC), Official Journal of the European Communities (OJEC), L 40, of 11.2.1989, p 12, as amended by Council Directive 93/68/EEC, OJEC, L 220 of 30.8.1993, p 1
2. Regulation (EU) No 305/2011 of the European Parliament and of the Council of 9 March 2011 laying down harmonised conditions for the marketing of construction products and repealing Council Directive 89/106/EEC. (Text with EEA relevance). Official Journal of the European Union (OJEU), L 88, 4.4.2011, p 5
3. Proposal for a Regulation of the European Parliament and of the Council laying down harmonised conditions for the marketing of the construction products (presented by the Commission). European Commission, 23.5.2008. COM(2008) 311 final
4. http://ec.europa.eu/enterprise/sectors/construction/index_en.htm
5. Regulation (EC) No 764/2008 of the European Parliament and of the Council of 9 July 2008 laying down procedures relating to the application of certain national technical rules to products lawfully marketed in another Member State and repealing Decision No 3052/95/EC. (Text with EEA relevance). Official Journal of the European Union (OJEU), L 218, 13.8.2008, p 21
6. Regulation (EC) No 765/2008 of the European Parliament and of the Council of 9 July 2008 setting out the requirements for accreditation and market surveillance relating to the marketing of products and repealing Regulation (EEC) No 339/93. (Text with EEA relevance). Official Journal of the European Union (OJEU), L 218, 13.8.2008, p 30
7. Decision No 768/2008/EC of the European Parliament and of the Council of 9 July 2008 on a common framework for the marketing of products, and repealing Council Decision 93/465/EEC. (Text with EEA relevance). Official Journal of the European Union (OJEU), L 218, 13.8.2008, p 82
8. Commission implementing Regulation (EU) No 1062/2013 of 30 October 2013 on the format of the European Technical Assessment for construction products. Official Journal of the European Union (OJEU), L 289, 31.10.2013, p 42
9. Commission Delegated Regulation (EU) No 157/2014 of 30 October 2013 on the conditions for making a declaration of performance on construction products available on a website. Official Journal of the European Union (OJEU), L 52, 21.2.2014, p 1
10. Commission Delegated Regulation (EU) No 574/2014 of 21 February 2014 amending Annex III to Regulation (EU) No 305/2011 of the European Parliament and of the Council on the model to be used for drawing up a declaration of performance on construction products. Official Journal of the European Union (OJEU), L 159, 28.05.2014, p 41
11. Commission Delegated Regulation (EU) No 568/2014 of 18 February 2014 amending Annex V to Regulation (EU) No 305/2011 of the European Parliament and of the Council as regards the assessment and verification of constancy of performance of construction products. Official Journal of the European Union (OJEU), L 157, 27.05.2014, p 76
12. European Committee for Standardization (CEN)/Construction Sector Standardization—guidance document. Implementation of the Construction Products Regulation (CPR) in harmonized standards. Working Document TF N 530 Rev.2. 13.04.2012
13. |PT|—Laws, Decree-Laws, etc.—Regulamento Geral das Edificações Urbanas (general building regulation). Decree no. 38 382, of 7 August 1951, and subsequent amendments
14. |PT|—Laws, Decree-Laws, etc.—Decree-Law no. 50/2008 of 19th of March, amending article 17 of the general building regulation and establishing a new legal framework for LNEC technical approvals
15. |PT|—Laws, Decree-Laws, etc.—Decree-Law no. 390/2007 of 10th December, establishing the mandatory certification for reinforcing steel for concrete
16. |PT|—Laws, Decree-Laws, etc.—Decree-Law no. 28/2007 of 12th February, establishing the mandatory certification for prestressing steel
17. European Committee for Standardization (CEN)—Quality management systems. Requirements (ISO 9001:2008). European Standard EN ISO 9001:2008

Aggregates

20

José Neves, António Correia Diogo, Ana Cristina Freire,
and Jorge de Brito

Abstract

Aggregates are basic materials intensively used in civil engineering works and transport infrastructures construction. These materials could be used on their own nature or in combination with a cementitious material. This chapter describes the main properties of the aggregates, including geometrical, physical, mechanical, chemical and environmental characteristics. The requirements of aggregates to be used in buildings and bridges (structural concrete) and infrastructures of transport are described separately, strongly relying on the technical specifications valid for each application type. The most relevant technical specifications concerning the use of aggregates in buildings and bridges are the standard specification for concrete aggregates. In the case of transport infrastructures, the general characteristics and the most important functions and applicable technical specifications are described for unbound granular layers for road and airport pavements and for use in construction of railway track.

Keywords

Pavement • Road • Airport • Railway track • Unbound granular material • Bound granular material • Concrete • Aggregate • Natural aggregate • Manufactured

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aggregate • Recycled aggregate • Coarse aggregate • Fine aggregate • Filler aggregate • Added filler

20.1 Aggregate Properties

20.1.1 Introduction to Aggregates

By definition, aggregates are granular mineral particles, used alone (dry aggregates) or dispersed in a fluid medium (wet aggregates) [1–4]. In some circumstances, the fluid medium is constituted by a suspension of a cementing material in water, which becomes solid as a result of a number of chemical reactions (hydration) that take place after mixing, and a concrete is formed [4]. In other cases, the "cementing material" is constituted by one or more poly-functional monomers which become solid due to polymerisation ("cure"), and a composite is formed [5]. A third situation is the one where the fluid medium is chemically inert and in such amount that the dispersion behaves like a fluid ("fluidisation"); in this case, "fluidised bed" is the current designation. Dry and wet granular materials present very distinct behaviour and properties, as we will see below.

Conventional aggregates are natural or manufactured materials used in civil engineering work and road construction either on their own nature (unbound aggregates) or in combination with a cementitious material (bound aggregates). According to EN 13242 [S-1], a natural aggregate is an aggregate from mineral sources that has been subjected to nothing else than mechanical processing. A manufactured aggregate is an aggregate of mineral origin resulting from an industrial process involving thermal or other modification.

Perhaps the first reference to flow properties of granular materials can be found in the poem "De Rerum Natura" by Lucretius (Titus Lucretius Carus, 99 BC-55 BC): To suck the poppyseeds from palm of hand is quite as easy as drinking water down (Liber II, 451–455). In modern language one could say that a situation of flow in a gas-fluidised bed was considered.

Aggregates are granular materials. Granular materials can be found everywhere, and they present some strange properties, either at rest or under flow conditions [1, 6–9]. Let us look at some examples of the peculiar behaviour of granular materials.

1. Dry granular material (e.g. sand) is discharged at some place over a flat horizontal surface, and a conical sand stack is formed.
   (a) The first peculiarity involves the pressure exerted by the conical sand pile on the floor:
      - If the force exerted at every contact point of the bottom granular layer with the flat surface is measured, an exponential distribution of force is found. The pressure at every "point" (by taking the force exerted by the grain at that contact point on the ground, and dividing it by the area of contact of that grain) presents huge fluctuations from place to place, and an overall exponential distribution is found.

- If the (average) pressure is measured over a contact area much greater than the cross section of a grain but much smaller than the bottom area of the sand pile, a constant value is found everywhere; this value does not depend on the height of the sand pile at that particular place, except very close to the border of the mound.

(b) The slope of the sand heap depends somewhat on the way the deposition of the sand was performed. By definition, the steepest angle of descent relative to the horizontal plane is called the angle of repose θ_{rep}.

- For θ_{rep} smaller than a critical value θ_{Max}, called the critical angle of repose, the sand pile remains at rest.
- For θ higher than θ_{Max}, the sand pile turns to be unstable and an avalanche is produced at the mound surface. This avalanche only involves the granular particles very close to the surface; the depth of the boundary layer which separates the flowing granular material from the one at rest is small.
- Multiple collisions occur between particles at the avalanche. The interactions between flowing grains are dissipative; granular flows require an external driving force (e.g. gravity) to persist. The avalanche stops when $\theta_{\text{rep}} = \theta_{\text{min}} < \theta_{\text{Max}}$.
- This pattern is typical of hysteresis: the output θ_{rep} depends not only on the current input but also on the history of past inputs.

(c) The same phenomenon occurs if a cylindrical drum is filled up with dry particles (e.g. sand) until about half height; the major axis of the cylinder is then turned to horizontal, and the drum started rotating very slowly, step by step, around the major axis (in the horizontal), as shown in Fig. 20.1. The step amplitude should be also very small (e.g. 50 mrad).

- The drum is prepared in such way that at time $t = 0$, all particles are at rest, and the free surface of the sand is horizontal. At $t = 0$ the angle between the free surface and the horizontal (embankment angle) is $\theta = 0$.
- For $t \geq 0$, all grains inside the drum remains at rest; the angle θ starts increasing stepwise from 0 up to a value $\theta = \theta_{\text{rot}}$.
- At $\theta = \theta_{\text{rot}}$ an avalanche is produced; when the granular material returns to the rest state, the angle of embankment drops to the value of the angle of repose $\theta_{\text{rep}} < \theta_{\text{rot}}$. The difference $(\theta_{\text{rot}} - \theta_{\text{rep}})$ is called the relaxation angle.
- As the stepwise rotation continues, the same phenomenon is repeated and the angle of repose θ continues oscillating between θ_{rep} and θ_{rot}. Again hysteresis is found.
- The same pattern is observed if the drum rotates continuously at low enough speed (e.g. one rotation in a few minutes).
- At higher speeds, the free surface of the sand is no more a plane surface and takes an S-shaped profile.

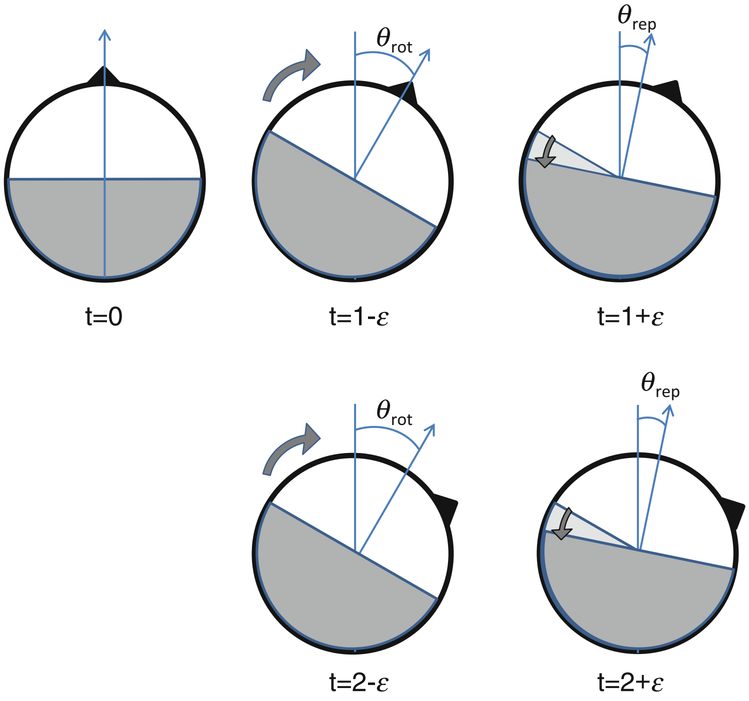
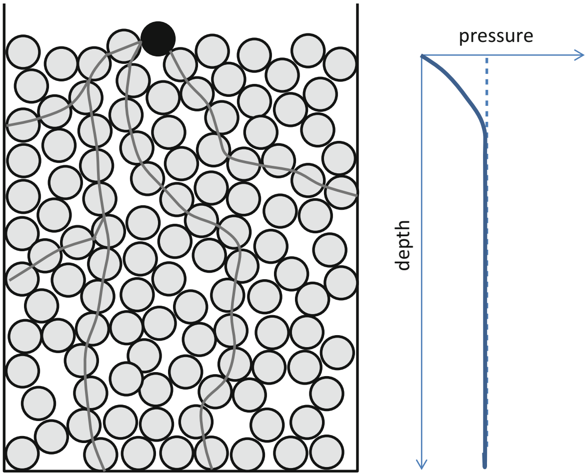


Fig. 20.1 Hysteresis in a rotating drum

2. Granular material is fed from the top of a tall cylindrical silo. There is an increase of the pressure at the bottom of the silo immediately after the silo starts being fed. Very soon the pressure attains a constant value, which remains the same until the silo is full. This constant value does not depend on the height of the granular material in the silo, provided the silo is tall enough.

   This peculiar behaviour is a consequence of the way grains interact in dry granular media. In a dry granular medium, at rest, the particle to particle interactions only result from the existence of static friction at the contact points between grains. Therefore, the interactions between contiguous grains are short-range, non-cohesive and dissipative. Moreover, one granular particle can only propagate stress if it is in contact with two or more other particles; the "efficiency" in stress transmission to other grains is expected to be strongly dependent on the particular geometric disposition of the contact points between that particular particle and the neighbour particles (see Fig. 20.2). Therefore, particle X_1 at the top of one silo can only interact with particle X_n somewhere below, provided a continuous chain of point contacts is able to transmit stress forces from particle X_1 to X_n: particle X_1 is in contact with particle X_2 and is able to transmit stress to it, particle X_2 is in contact with particle X_3 and is able to transmit stress to it, and so on up to particle X_n. These chains of transmission of stress forces are called "force chains"; some force chains are represented in Fig. 20.2. Force chains between particles can be interrupted by different ways,

Fig. 20.2 Chains of force. Variation of pressure with depth in a silo



e.g. if X_n is in contact with the walls of the container. Therefore, in a granular pile, each particle has a very limited number of contacts with its neighbours; the effective stress at any given particle depends on the number, strength and geometry of those contacts, so a wide distribution of force is expected among particles, and an exponential distribution law should be a good guess. In a silo, the weight of the granular content is supported by the walls and by a network of force chains for which only a limited amount of particles contribute, as shown in Fig. 20.2. As the silo is filled with more and more materials, the probability of force chains starting at the top will attain the bottom is reduced: most of the weight will be supported by the walls (silos collapse at the walls…).

It is interesting to mention that the basic laws of solid friction are clearly exposed in the papers left by Leonardo da Vinci (1452–1519) [10], and they were later rediscovered by Amontons (1663–1705) [11] and by Coulomb (1736–1806) [12]. A number of practical applications could be found later, based on the so-called Amontons-Coulomb laws of friction. Nevertheless, a clear understanding of the physics supporting the mechanics (statics, kinematics and dynamics) of granular media could have only been achieved in the last 30 years.

3. Let us return now to the silo considered before, and let us start to discharge the granular material from the bottom of the silo through a hopper.
   (a) The mass flow rate is (approximately) constant and it is independent of the height of granular material in the silo.
   (b) There is a finite probability that the granular flow becomes blocked at some time after the start-up of the granular flow (see Fig. 20.3). This is an example of the jamming transition. The flow is jammed due to the formation of a vault in the mouth of the hopper; the flow can only be restored after removal of the "cornerstone" (coloured in dark grey). The probability of the formation of such vaults (or arches) increases as the diameter of the mouth decreases [1, 7, 9].

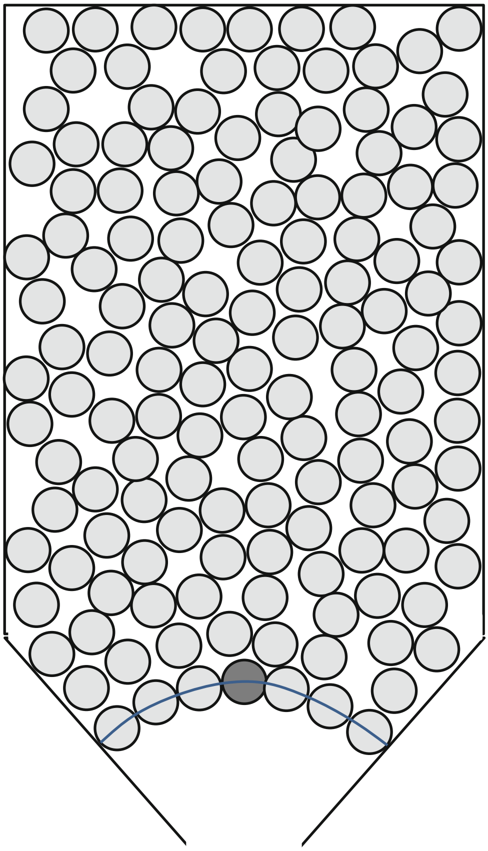


Fig. 20.3 Jamming by formation of a vault in the mouth of a hopper

Another peculiar phenomenon is segregation. The free energy of a mixture of two different molecular species includes a term $(-T\,\Delta S_{\text{comb}})$, where ΔS_{comb} is the combinatory entropy and T is the absolute temperature. An increase in ΔS_{comb} lowers the free energy, so it favours mixing. Granular materials at rest behave like thermodynamic systems at a temperature close to zero (0 K). Since $(-T\,\Delta S_{\text{comb}})$ is very close to 0, mixing has little or no effect in lowering the total free energy [7].

4. A tall vertical cylindrical container is first filled with grains of different sizes and densities, and then it is shaken in the vertical direction. Both segregation and convection occur: as time goes by, particles of different sizes tend to separate the largest particles move to the top and the smallest ones to the bottom, irrespective of their densities.
5. The same container (or a drum) is turned to the horizontal and slowly rotated around the major axis. Again, particle segregation occurs: particles separate into different regions (bands), sharply delineated; for each band, the critical angle of repose θ_{Max} is constant.

6. A vertical container filled up to height h_0 with particles of different sizes is shaken in the vertical direction for a sufficient long time. Shaking or vibrating the granular medium increases the particle mobility and plays a role equivalent to an increase of temperature in common liquids or gases: in fact, the root mean square of particle velocity fluctuations is analogous to thermodynamic temperature. In general, the height of the granular material in the silo slowly decreases as the time of shaking increases, so the material becomes more compact with time. This relaxation process is very slow: the increase of compacity (the fraction of volume filled by the grains) is proportional to the logarithm of time (or to the logarithm of number of shaking cycles) [6, 13].

There is a strong difference in behaviour between dry and wet granular materials [4, 14].

As mentioned before, in dry granular materials the interactions between grains only result from static friction at the contacts between grains: they are short range, non-cohesive and dissipative. On the other hand, in wet granular materials some liquid is present, wetting the grains and filling the pore volume. The liquid is expected to induce cohesion between grains mediated by surface tension, in two ways. The first way involves the formation of liquid bridges at the contact points between pairs of grains. A meniscus between air and liquid with positive curvature generates a positive pressure difference between the air and the liquid (suction), given by the Young-Laplace equation. The attracting force induced by the liquid bridge between two identical spheres is the sum of two contributions: one due to wetting of the sphere caps by the liquid and the other involves suction due to the liquid menisci (see Fig. 20.4). The second way deals with finite granular clusters filled with liquid; the boundary of these clusters includes liquid menisci and particle caps. Due to suction, the liquid pressure inside the clusters is smaller than the air pressure outside the clusters, and a cohesive interaction among particles results.

The calculation of the force that keeps two spheres in contact by a capillary bridge involves some sophistication [15]. A rough estimate of the radius R of the sphere such that capillary force and gravity are equal is [1]:

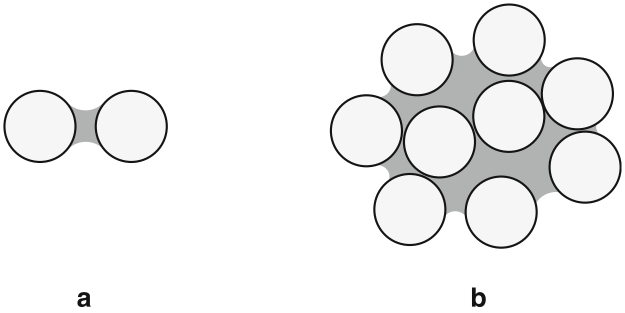


Fig. 20.4 (**a**) Attraction of two spheres by formation of a bridge. (**b**) Attraction in a wet swarm mediated by liquid menisci

$$R^2 \approx \frac{4 \cdot \gamma_{\mathrm{lg}} \cdot \alpha}{g \cdot \rho_{\mathrm{sphere}}}, \tag{20.1}$$

where γ_{lg} is the surface tension at the liquid–air interface, ρ is the spherical particle density and α is the ratio between the radius of the meniscus and the radius R of the particle. By putting values in Eq. 20.1, some interesting results may be guessed. For water, $\gamma_{\mathrm{lg}} = 72$ mN/m, $\rho = 2 \times 10^3$ kg/m^3 and $\alpha = 1$ (~15 % water content), particles remain stuck for radius R up to ~4 mm. For powders (particles smaller than 100 μm), particles are kept stuck for $\alpha \sim 7 \times 10^{-4}$, which means that a tiny moisture content (<2 %) may produce severe changes in the flow behaviour of such materials.

The properties of dry and wet granular materials are very different, as seen by comparing dry and wet sand [1, 2]. Dry sand can be easily poured like a liquid (as noticed by Lucretius one century BC). Wet sand looks more like a solid. The angle of repose of a dry sand pile is finite, well defined, and varies in a relatively narrow range; the angle of repose of wet sand can be 90° or even more, as seen in sandcastles. Wet sand can be moulded and keep a variety of shapes since there is cohesion among particles induced by capillarity.

According to the liquid content, four regimes of liquid content can be found in wet granular materials [14] (see Fig. 20.5):

- *Pendular state*. The amount of liquid present is small, so only a number of liquid bridges between pairs of close particles are formed. Cohesive forces act exclusively through the liquid bridges.
- *Funicular state*. Some pores are fully saturated by liquid and finite granular clusters start to be formed; some other pores remain filled with air and connected one another by liquid bridges. Granular clusters and liquid bridges both contribute to the overall cohesion.
- *Capillary state*. Almost all pores are filled with liquid; clusters of granular material with filled pores are dominant. The main contribution to cohesion is provided by the suction due to menisci at the surface of the particle clusters.
- *Slurry state*. All pores are filled with liquid; interparticle cohesion is absent.

Suction (measured by the pressure difference between air and the liquid) is strongly dependent of the liquid content. A log plot of suction versus the liquid content presents the following qualitative behaviour (see Fig. 20.6). It is maximum

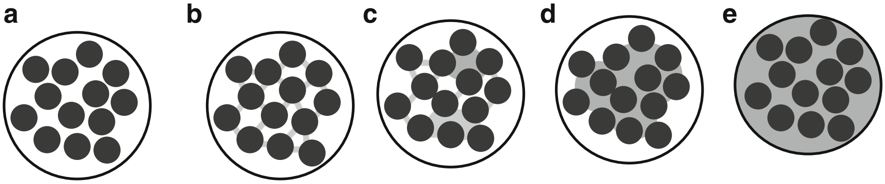


Fig. 20.5 Regimes of liquid content in granular materials: (**a**) dry state; (**b**) pendular; (**c**) funicular; (**d**) capillary; (**e**) slurry

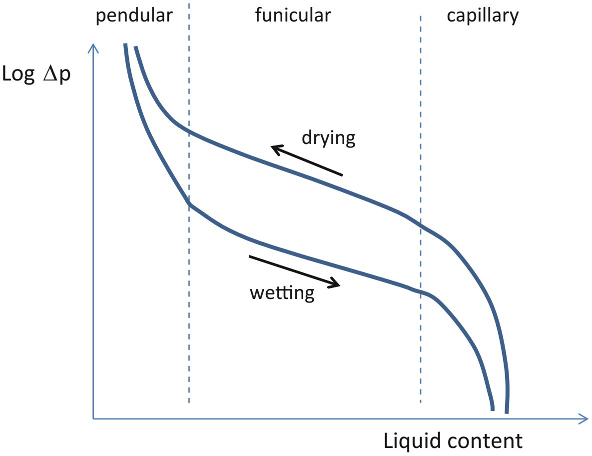


Fig. 20.6 Suction versus liquid content in wet granular materials

at very low liquid content, and strongly decreases as the pendular regime is crossed. Then a “plateau” is found, which corresponds to the funicular regime. The transition to the capillary regime is again marked by a strong further decrease of the suction.

20.1.2 Properties of Aggregates

The main factors controlling the physical behaviour of granular materials are [4, 6, 8]:

(a) Compacity
(b) Particle size distribution
(c) Friction between particles

Compacity, or the fraction of total volume filled with particles, is one of the most important characteristics of granular materials. Compacity is strongly related to the grain-size distribution or gradation, but it also depends on the actual packing density of the granular particles. In some cases, e.g. transport of granular material, maximum compacity is desired, and the grain-size distributions which minimise the volume of voids may be computed with reasonable approximation once the geometric shape of the particles is known (see Fig. 20.7a). More often an optimisation process is required. In concrete, too much fines content requires an excessive amount of cement to coat the particles and does not improve mechanical resistance (see Fig. 20.7b). An analogous optimisation is required in composites.

Friction between particles is the main factor involved in particle-particle interaction in dry granular materials. It depends on the shape of the particles and on the surface texture. Changes in size (broken particles), shape (e.g. rounded particles) or surface texture (e.g. surface polishing) can affect strongly the performance of the granular material or composite and reduce the lifetime of the parts or components in which it is included. A number of physical properties are involved in such factors:

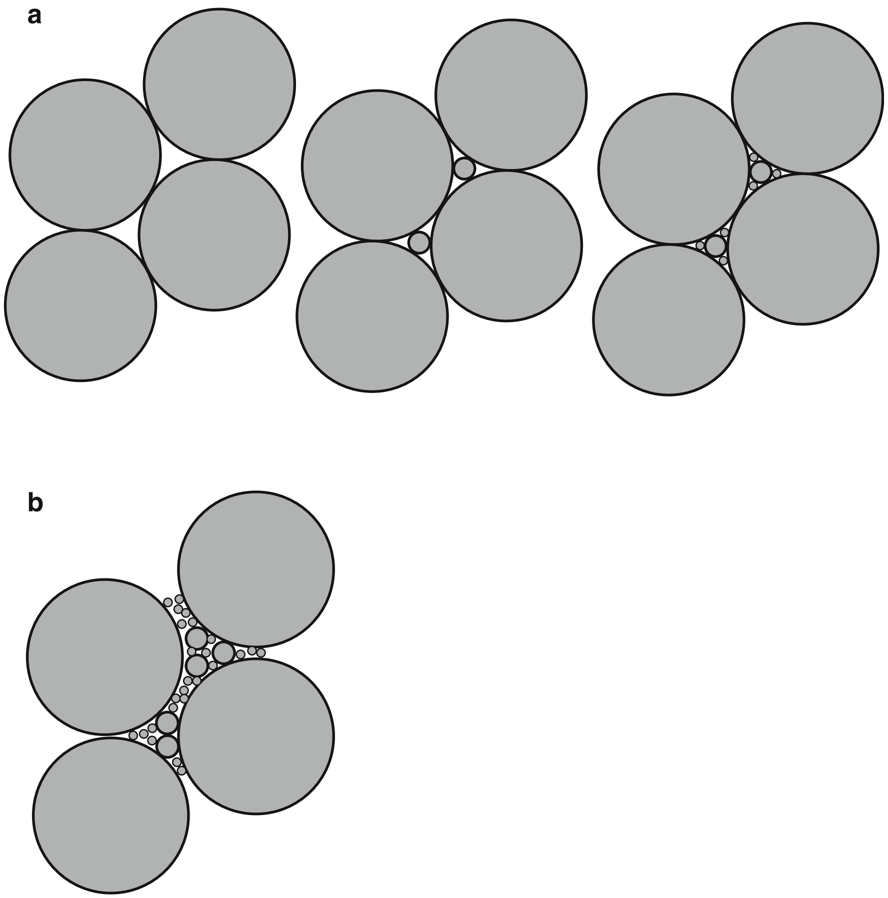


Fig. 20.7 (**a**) Filling of space by particles with different sizes, in granular materials. (**b**) Effect of excessive amount of fines: loss of cohesion

- Hardness is an important factor controlling the interparticle friction; it is also involved in resistance to wear.
- Wear is probably the main factor involved into changes of the surface texture and shape of the particles (polishing); it may also affect the particle size distribution, mainly with regard to the fines content. Wear is particularly important for granular materials submitted to periodic loads (pavements) or to transport (flows).
- Ambient conditions (weather, aggressive atmospheres, etc.) affect the surface texture and the particle size distribution.
- Deleterious substances may be particularly harmful in aggregates to be mixed to curing resins (composites) or with cements. They may affect strongly the particle surface and, by consequence, the adhesion between particles and the matrix in composites, or the adhesion between aggregate and cement in concretes.

– Crushing strength is the compressive load that particles can carry before breaking. Particle crushing strongly affects the particle size distribution both in the large particles side and in the fines content side.

For granular materials as well as for porous materials, density, porosity, volume, etc., are concepts that may be ambiguous and need some clarification. Consider an ensemble of particles or solid matter limited by the closed surface S. Inside S there are voids (cavities, pores, holes, etc.) and solid matter; the voids can be filled by fluids, but solid matter cannot. The volume V associated to the closed surface S is called the envelope volume and it includes: solid matter, surface roughness, open pores and closed pores. Surface irregularities with characteristic diameter ϕ and depth ℓ are classified as surface roughness if $\ell < \phi$ and as open pores otherwise. Pore volume includes closed pores (totally isolated from outer surface S) and open pores (connected to the outer surface S). Open pores can be passing pores (permeable to liquids, both extremities are connected to the outer surface) and blind pores (one extremity connected to the surface, cannot be crossed by liquids). The different kinds of volume are presented in Table 20.1.

For wet granular materials, in density calculations, one must take into account that, besides the granular material, the constituent particles may also be porous. Therefore, the added liquid (e.g. water) may fill the void space among grains as well as the open pores inside the particles of aggregate; moreover, some liquid is expected to wet the particles surface. All these amounts of water have to be taken into consideration in computing the density of the wet aggregate. In general, three moisture conditions have to be considered:

(a) Dry granular density: (dry mass of aggregate)/(envelope volume)
(b) Saturated (surface-dry) density: (dry mass of aggregate + mass of liquid to fill all open porosity of aggregate particles)/(envelope volume)
(c) Wet (surface-wet) density: (dry mass of aggregate + mass of liquid filling all open pores of particles + mass of liquid wetting all aggregate particles)/(envelope volume)

Table 20.1 Different kinds of volume definitions for porous materials

Definitions	Solid matter	Open pores	Closed pores	Surface roughness
Absolute volume (BSI)	x			
Apparent volume (BSI)	x		x	
Global volume (ASTM D3766)	x	x	x	x
Envelope volume (BSI)	x	x	x	x
Envelope volume (ASTM D3766)	x	x	x	x
Geometric volume (calculated)	x	x	x	x
Skeletal volume (ASTM D3766)	x		x	
True volume (BSI)	x			

In practice, saturated surface-dry particles look moist but not shiny and surface-wet aggregate particles look shiny due to the wetting layer of liquid on the surface of the particle.

20.1.3 Aggregate Tests

The most important properties of the aggregates for engineering purposes are obtained from experimental tests. Within the EU, the Comité Européen de Normalisation (CEN) has the responsibility for normalising the different national standards and preparing agreed European ones. Requirements for the various uses of aggregates are specified in the following European standards:

- EN 12620, aggregates for concrete [S-2]
- EN 13043, aggregates for bituminous mixtures and surface treatments for roads, airfields and other trafficked areas [S-3]
- EN 13055, lightweight aggregates [S-4]
- EN 13139, aggregates for mortar [S-5]
- EN 13242, aggregates for unbound and hydraulically bound materials for use in civil engineering work and road construction [S-1]
- EN 13383-1, armourstone [S-6]
- EN 13450, aggregates for railway ballast [S-7]

Aggregates used in construction should comply with all the requirements of these European standards. These documents are based on series of normative references indispensable for its application and covering the following properties of aggregates:

- Tests for general properties of aggregates (EN 932)
- Tests for geometrical properties of aggregates (EN 933)
- Tests for mechanical and physical properties of aggregates (EN 1097)
- Tests for thermal and weathering properties of aggregates (EN 1367)
- Tests for chemical properties of aggregates (EN 1744)

In the case of the general properties of aggregates, the test methods include the following parts: methods for sampling (EN 932-1 [S-8]), methods for reducing laboratory samples (EN 932-2 [S-9]), procedure and terminology for simplified petrographic description (EN 932-3 [S-10]), quantitative and qualitative system for description and petrography (EN 932-4 [S-11]), common equipment and calibration (EN 932-5 [S-12]), definitions of repeatability and reproducibility (EN 932-6 [S-13]), conformity criteria for test results (EN 932-7 [S-14]).

Geometrical properties of aggregates includes: determination of particle size distribution (sieving method) (EN 933-1 [S-15]), determination of particle size distribution (test sieves); nominal size of apertures (EN 933-2 [S-16]), determination of particle shape (flakiness index) (EN 933-3 [S-17]), determination of particle shape (shape index) (EN 933-4 [S-18]), determination of percentage of crushed and broken surfaces in coarse aggregate particles (EN 933-5 [S-19]), assessment of surface characteristics (flow coefficient of aggregates) (EN 933-6 [S-20]), determination of shell content (percentage of shells in coarse aggregates) (EN 933-7 [S-21]), assessment of fines (sand equivalent test) (EN 933-8 [S-22]), assessment of fines (methylene blue test) (EN 933-9 [S-23]), assessment of fines (grading of filler aggregates) (air jet sieving) (EN 933-10 [S-24]), and classification test for the constituents of coarse-recycled aggregate (EN 933-11 [S-25]).

In terms of the mechanical and physical properties of aggregates, the following parts of the test methods are available: determination of the resistance to wear (micro-Deval) (EN 1097-1 [S-26]), methods for the determination of resistance to fragmentation (EN 1097-2 [S-27]), determination of loose bulk density and voids (EN 1097-3 [S-28]), determination of the voids of the dry compacted filler (EN 1097-4 [S-29]), determination of the water content by drying in a ventilated oven (EN 1097-5 [S-30]), determination of particle density and water absorption (EN 1097-6 [S-31]), determination of the particle density of filler (Pycnometer method) (EN 10976-7 [S-32]), determination of the polished stone value (PSV) (EN 1097-8 [S-33]), determination of the resistance to wear by abrasion from studded tyres (Nordic test) (EN 1097-9 [S-34]), determination of water suction height (EN 1097-10 [S-35]), determination of compressibility and confined compressive strength of lightweight aggregates (EN 10976-11 [S-36]).

Thermal and weathering properties of aggregates are determined by the following parts of the test methods: determination of resistance to freezing and thawing (EN 1367-1 [S-37]), magnesium sulphate test (EN 1367-2 [S-38]), boiling test for “Sonnenbrand basalt” (EN 1367-3 [S-39]), determination of drying shrinkage (EN 1367-4 [S-40]), determination of resistance to thermal shock (EN 1367-5 [S-41]), determination of resistance to freezing and thawing in the presence of salt (NaCl) (EN 1367-6 [S-42]), determination of resistance to freezing and thawing of lightweight aggregates (EN 1367-7 [S-43]), determination of resistance to disintegration of lightweight aggregates (EN 1367-8 [S-44]).

Test methods for chemical properties of aggregates are described in the following parts: chemical analysis (EN 1744-1 [S-45]), preparation of eluates by leaching of aggregates (EN 1744-3 [S-46]), determination of water susceptibility of fillers for bituminous mixtures (EN 1744-4 [S-47]), determination of acid-soluble chloride salts (EN 1744-5 [S-48]), determination of the influence of recycled aggregate extract on the initial setting time of the cement (EN 1744-6 [S-49]), determination of loss of ignition of Municipal Incinerator Bottom Ash Aggregate (MIBA Aggregate) (EN 1744-7 [S-50]), sorting test to determine metal content of MIBA Aggregates (EN 1744-8 [S-51]).

20.2 Production and Quality Control

20.2.1 Natural Aggregates

Production of aggregates includes different processes since the extraction of the material source until the particle grain-size selection.

Natural aggregates are quarried from solid rock formations with different origins: igneous, sedimentary and metamorphic.

Igneous rocks are formed by the cooling of the magma material resulted from a volcanic eruption. Two types of igneous rocks are possible: extrusive or volcanic rocks formed by the rapidly cooling of the magma at the earth's surface and mainly characterised by a very fine or glassy texture; intrusive rocks are the result of a slowly cooling of the magma and they have a coarse crystalline texture, with crystals clearly visible to the naked eye. Most common volcanic rock is the basalt, very dark in colour and with pyroxene and olivine crystals. Tuff is an accumulation of fine-grained, volcanic, fragmentary material, usually well indurated. Breccia is also a frequent volcanic rock formed by the brecciation and consolidation of lava. Granite is a typically intrusive rock containing alkali feldspars and quartz, with mica (biotite and/or muscovite). Other igneous rocks could originate natural aggregates, as syenite, diorite and dolerite.

Sedimentary rocks are formed at the earth's surface by the accumulation or precipitation of the products from physical weathering and erosion of pre-existing rocks. The consolidation of these fragments originates clastic sedimentary rocks (e.g. sandstone, conglomerate). If the accumulation of skeletons of organisms or the chemical solution and precipitation lithified into rock, biogenic or chemical rocks are formed and designated as non-clastic (e.g. limestone, chalk). Sedimentary rocks are usually and typically layered as the result of these processes of origin.

Metamorphic rocks are formed from pre-existing rocks. The action of heat and/or pressure in the earth's crust can cause mineralogical and structural transformation. Metamorphic rocks frequently have anisotropic texture and typical examples are gneiss, schist and marble.

Aggregates derived from natural and unconsolidated deposits consist mainly of mineral particles and rock fragments. Sand and gravel are the main resources extracted from these deposits, with important applications in the construction (e.g. concrete). The general description of the aggregate should be based on the main components, rock or mineral, predominant in the material. For example, basaltic gravel is a gravel material in which more than 50 % of the particles consist of fragments with a basaltic origin. If a no single type of fragment is predominant, the aggregate is a heterogeneous material. The origin of the deposits could be diverse, e.g. alluvium, beach deposit, slope scree, till and glaciofluvial deposit.

Alluvial deposits (rivers, lakes and ponds) are common natural aggregate sources (sand and gravel). However, the most production of natural aggregates worldwide is from hard rock sources found in quarries and underground mines. The manufacturing process of the aggregates in a quarry generally comprises the following phases:

- Preparation of the rock mass and design of the rock blasting
- Extraction of the rock and its transport to the crushing plant
- Primary processing and storage of the resulting product
- Subsequent processes to obtain the aggregates and their storage in the quarry
- Transport of the aggregate to the final destination

In the phase of preparation of the rock mass, the works related to the cleaning of all the quarry area from the vegetation and other materials detrimental to the final quality of the aggregates are included. The design of the rock blasting is related to the choice of the type and amount of explosive to be used to extract the rock and to the mesh geometry of the holes where the explosive is introduced.

The extraction of the rock is usually carried out by the use of explosives. The result from this destructive process is rock blocks with different dimensions that, after a preliminary selection, are transported to the crushing plant. When very large pieces of rock blocks are obtained, it is necessary to reduce them in order to obtain smaller blocks compatible with the crusher dimension. This complementary process could be performed by a secondary blasting and/or by a hydraulic hammer.

When the rock blocks are transported to the crushing plant, a primary processing is implemented consisting on a primarily selection of the material and on a fragmentation stage. The resulting material from this phase is stored to serve the subsequent phases.

Subsequent processes are essentially composed by crushing and screening. Crushing involves the continuous process of size reduction of the block rocks by the use of compression or impact crushers. The type of crusher influences the size and the shape of the aggregate result. In order to obtain aggregates with different sizes, the screening process, using vibrating screens, should be implemented in conjunction with a certain number of crushing stages. It is common a tertiary stage of the aggregate reduction in order to finally obtain all the commercial grain sizes. All aggregate fractions produced in the crushing plant stay in storage until required.

20.2.2 Recycled Aggregates

A recycled aggregate is an aggregate resulting from the processing of inorganic or mineral material previously used in construction. The need for a sustainable engineering construction and maintenance calls for more and more news and innovating techniques and materials. In general, the re-usage of construction and demolition waste (CDW) has the double purpose of promoting, on the one hand, the reduction of the depletion of natural resources and the minimisation of the large amount of waste to landfills sites and, on the other hand, the production of recycled aggregates. This is the case of recycled aggregates CDW (e.g. concrete, stone, ceramic tiles) obtained from the construction and demolition of buildings, bridges and other structures in the domain of civil engineering. Generally, CDW composition includes inert (concrete, bricks, tiles, asphalt stones, soil), organic (paper, wood) and composite materials (plasters, electric material). Other origins for recycled aggregates could be possible as natural and industrial sub-products derived from several human activities (steel slag, fly-ash, incinerated refuse).

In the case of CDW, important developments of production processes were attained and have allowed a better quality of recycled materials in the most recent years. In fact, the nature of the original CDW has an important role on the final quality of recycled aggregates, but also the demolition, selection and crushing processes have a crucial influence on its composition and quality.

The most common processes of CDW are done by either mobile or fixed recycled plants. In both cases, it is desirable to have the plant localisation near the origin and the final destination of CDW. If fixed plants give a more accurate quality and diversity of the aggregate, instead its costs of installation and operation, and CDW transport, achieve huge values. Mobile plants are very frequent and have the great advantage of a lower cost of operation and of CDW transports.

In the case of the production of recycled aggregates from CDW, three phases could be considered:

- Demolition and collection
- Screening
- Crushing

The materials resulting from the "primary demolition" have to be reduced in size in order to facilitate the transportation for recycling. For this purpose, sprayers, hydraulic and mechanical, in order to separate the steel presented in the concrete are used. The "selective demolition", taking place yet in the origin of the waste, is very important in order to promote the segregation of the materials, safely and efficiently, according to their characteristics. Magnetic and dry separations are technical procedures to complement demolition and collection of recycled aggregates. Screening and crushing procedures are similar to those performed in natural aggregates.

20.2.3 Quality Control and CE Marking

The global quality of the aggregates not only depends on the intrinsic properties of the rock source but is also associated with the global factory production process.

Actually, the Construction Products Regulation is the mandatory document to all European Union member states to CE marking products produced to harmonise European standards. In general, CE marking aims to ensure that construction products satisfy the requirements of the relevant European standards and are also safe to use, and those properties are guaranteed following a system which is common throughout Europe. Practically, it is necessary to declare a defined set of properties of the product, as required in the relevant European standard, and characteristics that will be measured and/or verified following a given procedure.

Aggregates are systematically used in building construction and infrastructures; therefore, they directly influence the quality and safety of the structures.

Manufacturers are solely responsible for the compliance of the aggregates with the terms of the regulation, either for trade or use. When a manufacturer identifies its aggregate with the CE mark, this means that the aggregate complies with the harmonised standards and therefore fulfils the essential requirements of the regulation. CE marking of aggregates is governed by Assessment of Conformity (AoC) system 2+, which requires the intervention of a notified body to perform a factory production control (FPC) audit. CE marking is a legal declaration by the manufacturer indicating the properties of the aggregates and their conformity with standard requirements, specified for each size of aggregate and depending on the application: aggregates for concrete; aggregates for bituminous mixtures and surface treatments for roads, airfields and other trafficked areas; lightweight aggregates for concrete, mortar and grout; lightweight aggregates for bituminous mixtures and surface treatments and for unbound and bound applications; aggregates for mortar; aggregates for unbound and hydraulically bound materials for use in civil engineering work and road construction; armour stone; and aggregates for railway ballast. European aggregate standards regarding each application are based on the use of categories and classes to define the properties of aggregates.

Requirements for the evaluation of conformity of the products to these European standards are given in EN 16236 [S-52], evaluation of conformity of aggregates. This European standard specifies both initial type testing (ITT) and FPC requirements for use during the evaluation and production of aggregates. When the adequate “conformity” clauses are applied, it forms part of the system for attestation of conformity and it provides the minimum level of ITT and FPC for CE marking.

The ITT procedures are based on the reference test methods and they have the function to guarantee that a particular aggregate product complies with the specified requirements. The FPC system requires control of the sourcing and processing of the aggregate combined with routine sampling and testing to provide ongoing assurance that the aggregate product continues to conform to those properties determined through ITT.

20.3 Applications and Technical Specifications

In this section the requirements of aggregates to be used in buildings and bridges (structural concrete) and infrastructures of transport are described separately, strongly relying on the technical specifications valid for each application type.

20.3.1 Buildings and Bridges

20.3.1.1 Scope

The most relevant technical specifications concerning the use of aggregates in buildings and bridges (structural concrete) are EN 12620 “Aggregates for concrete”

[S-2] and ASTM C33/C33M "Standard specification for concrete aggregates" [S-53].

These standards define the requirements demanded from aggregates suitable to be used in concrete production. The following description of these requirements follows the presentation sequence of EN 12620 [S-2]. For North American readership, the ASTM standards roughly equivalent to the European norms referred in the description are identified between parentheses right after.

After an introductory section about aggregates classification, the following sections describe the geometrical, chemical and physical requirements of aggregates for concrete.

20.3.1.2 Aggregates Classification

Aggregates for concrete may have several natural petrographic origins[1] (igneous, sedimentary and metamorphic), be manufactured (e.g. expanded clay or shale) and they may also be recycled (from crushed concrete, ceramic products, undifferentiated CDW and others).

In terms of size,[2] the aggregates may be classified as: coarse aggregate (larger aggregate sizes with D greater than or equal to 4 mm and d greater than or equal to 2 mm); fine aggregate (smaller aggregate sizes with D less than or equal to 4 mm); natural graded 0/8 mm aggregate (natural aggregate of glacial and/or fluvial origin with D less than or equal to 8 mm); all-in aggregate (a mixture of coarse and fine aggregate with $D \leq 45$ mm and $d = 0$); filler aggregate (aggregate, most of which passes a 0.063 mm sieve, which can be added to construction materials to provide certain properties); fines (particle size fraction of an aggregate which passes the 0.063 mm sieve).

In terms of oven-dried particle density,[3] the aggregates may be classified as: lightweight aggregate (aggregate with oven-dried particle density $\leq 2{,}000$ kg/m^3) [S-4, S-58]; normal aggregate (aggregate with oven-dried particle density higher than 2,000 kg/m^3 and lower than 3,000 kg/m^3); heavyweight aggregate (aggregate with oven-dried particle density $\geq 3{,}000$ kg/m^3).

20.3.1.3 Geometrical Requirements

The most relevant geometrical properties of aggregates for concrete are aggregate size, grading,[4] shape of coarse aggregate, shell content of coarse aggregate, fines content and quality.

Aggregate size is expressed as d/D as a function of the lower and upper sieve sizes. The sieve sizes are selected from a basic set, or the basic set plus set 1, or the

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[1] A simplified petrographic description can be performed according to EN 932-3 [S-9] (ASTM C295/C295M [S-54]).

[2] Aggregate size is defined in terms of lower (d) and upper (D) sieve sizes expressed as d/D.

[3] Determined according to EN 1097-6 [S-31] (ASTM C127 [S-55] and ASTM C128 [S-56]).

[4] Determined according to EN 933-1 [S-15] (ASTM C136 [S-57]).

Table 20.2 Sieve sizes for specifying aggregate sizes [1]

Basic set [mm]	Basic set plus set 1 [mm]	Basic set plus set 2 [mm]
0	0	0
1	1	1
2	2	2
4	4	4
–	5.6 (5)	–
–	–	6.3 (6)
8	8	8
–	–	10
–	11.2 (11)	–
–	–	12.5 (12)
–	–	14
16	16	16
–	–	20
–	22.4 (22)	–
31.5 (32)	31.5 (32)	31.5 (32)
–	–	40
–	45	–
63	63	63

Note: Rounded sizes shown in parentheses can be used as simplified descriptions of aggregate sizes

Table 20.3 General grading requirements [1]

		Percentage passing by mass					
Aggregate	Size	$2D$	$1.4D^{a,b}$	D^{c}	d^{b}	$d/2^{a,b}$	Category G*d*
Coarse	$D/d \leq 2$ or $D \leq 11.2$ mm	100	98–100	85–99	0–20	0–5	G_C85/20
		100	98–100	80–99	0–20	0–5	G_C80/20
	$D/d > 2$ and $D > 11.2$ mm	100	98–100	90–99	0–15	0–5	G_C90/15
Fine	$D \leq 4$ mm and $d = 0$	100	95–100	85–99	–	–	G_F85
Natural graded 0/8	$D = 8$ mm and $d = 0$	100	98–100	90–99	–	–	G_{NG}90
All-in	$D \leq 45$ mm and $d = 0$	100	98–100	90–99	–	–	G_A90
		100	98–100	85–99			G_A85

[a] Where the sieves calculated are not exact sieve numbers in the ISO 565 [S-59] R 20 series, then the next nearest sieve size shall be adopted

[b] For gap graded concrete or other special uses, additional requirements may be specified

[c] The percentage passing *D* may be greater than 99 % by mass but in such cases the producer shall document and declare the typical grading including the sieves *D*, *d*, *d*/2 and sieves in the basic set plus set 1 or basic set plus set 2 intermediate between *d* and *D*. Sieves with a ratio less than 1.4 times the next lower sieve may be excluded

[d] Other aggregate product standards have different requirements for categories

Table 20.4 Overall limits and tolerances for coarse aggregate grading at midsize sieves [1]

D/*d*$_0$	Midsize sieve [mm]	Overall limits and tolerances at midsize sieves (percentage passing by mass)		Category G$_T$
		Overall limits	Tolerances on producer's declared typical grading	
<4	*D*/1.4	25–70	±15	G$_T$15
≥4	*D*/2	25–70	±17.5	G$_T$17.5

Where the midsize sieve calculated as above is not an exact sieve size in the ISO 565 [5b] R20 series, then the nearest sieve in the series shall be used

Table 20.5 Tolerances on producer's declared typical grading for general use fine aggregates [1]

Sieve size [mm]	Tolerances in percentages passing by mass		
	0/4	0/2	0/1
4	±5[a]	–	–
2	–	±5[a]	–
1	±20	±20	±5[a]
0.250	±20	±25	±25
0.063[b]	±3	±5	±5

[a] Tolerances of ±5 are further limited by the requirements for the percentage passing *D* in Table 20.2

[b] In addition to the tolerances stated, the maximum value of the fines content for the category selected from Table 20.11 applies for the percentage passing the 0.063 mm sieve

Table 20.6 Sieve sizes for specifying aggregate sizes [1]

Sieve size [mm]	Tolerances (percentages passing by mass)
82	±5
1	±10
0.250	±10
0.125	±10
0.063	±3
82	±2

basic set plus set 2 (Table 20.2). A combination of sizes from set 1 and set 2 is not permissible. Furthermore, aggregate sizes shall have *D*/*d* not less than 1.4.

The grading of the aggregate must comply with the requirements in Tables 20.3, 20.4, 20.5, 20.6, 20.7, and 20.8, according to its aggregate size *d*/*D*.

When required, the shape of the coarse aggregates is determined in terms of the following parameters: flakiness index, according to EN 933-3 [S-17] (Table 20.9) (ASTM D4791 [S-60]); shape index, according to EN 933-4 [S-18] (Table 20.10) (ASTM D3398 [S-61]).

When required, the shell content of the coarse aggregates is determined according to EN 933-7 [8] (Table 20.11).

The fines content is determined according to EN 933-1 [S-15] (Table 20.12) (ASTM C136 [S-62]) and the fines quality, in terms of being considered non-harmful, is considered compliant if the four following conditions apply:

Table 20.7 Grading requirements for all-in aggregates [1]

Aggregate size [mm]		Overall limits of the sieves indicated below (percentage passing by mass)	
		40 ± 20	70 ± 20
Basic set plus set 1	Basic set plus set 2	For the sieve [mm]	
–	0/6,3	1	4
0/8	0/8	1	4
–	0/10	1	4
0/11.2 (11)	–	22	5.6 (5)
–	0/12.5 (12)	2	6.3 (6)
–	0/14	2	8
0/16	0/16	2	8
–	0/20	2	10
0/22.4 (22)	–	44	11.2 (11)
0/31.5 (32)	0/31.5 (32)	4	16
–	0/40	1	20
0/45	–	1	22.4 (22)

Note. Figures in parentheses can be used to provide simplified descriptions of aggregate sizes

Table 20.8 Grading requirements for filler aggregate [1]

Sieve size [mm]	Percentage passing by mass	
	Overall range for individual results	Producer's maximum declared range[a]
2	100	–
0.125	85–100	10
0.063	70–100	10

[a] Declared grading range on the basis of the last 20 values. 90 % of the results shall be within this range, but all the results shall be within the overall grading range (see *column 2* above)

Table 20.9 Categories for maximum values of flakiness index [1]

Flakiness index	Category FI
≤ 15	FI_{15}
≤ 20	FI_{20}
≤ 35	FI_{35}
≤ 50	FI_{50}
>50	FI_{Declared}
No requirement	FI_{NR}

- The total fines content of the fine aggregate is less than 3 % or other value according to the provisions valid in the place of use of the aggregate.
- The sand equivalent value (SE) when tested in accordance with EN 933-8 [S-22] (ASTM D2419 [S-63]) exceeds a specified lower limit (with a probability of 90 %).

Table 20.10 Categories for maximum values of shape index [1]

Shape index	Category SI
≤15	SI_{15}
≤20	SI_{20}
≤40	SI_{40}
≤55	SI_{55}
>55	$SI_{Declared}$
No requirement	SI_{NR}

Table 20.11 Category for maximum value of shell content of coarse aggregates [1]

Shell content [%]	Category SC
≤10	SC_{10}
>10	$SC_{Declared}$
No requirement	SC_{NR}

Table 20.12 Categories for maximum values of fines content [1]

Aggregate	0.063 mm sieve (percentage passing by mass)	Category f
Coarse aggregate	≤1.5	$f_{1.5}$
	≤4	f_4
	>4	$f_{Declared}$
	No requirement	f_{NR}
Natural graded 0/8 mm aggregate	≤3	f_3
	≤10	f_{10}
	≤16	f_{16}
	>16	$f_{Declared}$
	No requirement	f_{NR}
All-in aggregate	≤3	f_3
	≤11	f_{11}
	>11	$f_{Declared}$
	No requirement	f_{NR}
Fine aggregate	≤3	f_3
	≤10	f_{10}
	≤16	f_{16}
	≤22	f_{22}
	>22	$f_{Declared}$
	No requirement	f_{NR}

- The methylene blue test (MB) when tested in accordance with EN 933-9 [S-23] (AASHTO T330 [S-64] or ASTM C1777 [S-65]) gives a value less than a particular specified limit (with a probability of 90 %).
- Equivalence of performance with known satisfactory aggregate is established or there is evidence of satisfactory use with no experience of problems.

Table 20.13 Categories for maximum values of Los Angeles coefficients [1]

Los Angeles coefficient	Category LA
≤15	LA_{15}
≤20	LA_{20}
≤25	LA_{25}
≤30	LA_{30}
≤35	LA_{35}
≤40	LA_{40}
≤50	LA_{50}
>50	LA_{Declared}
No requirement	LA_{NR}

Table 20.14 Categories for maximum values of resistance to wear [1]

Micro-Deval coefficient	Category M_{DE}
≤10	$M_{DE}10$
≤15	$M_{DE}15$
≤20	$M_{D}E20$
≤25	$M_{DE}25$
≤35	$M_{DE}35$
>35	M_{DE}Declared
No requirement	M_{DE}NR

20.3.1.4 Physical Requirements

The most relevant physical properties of aggregates for concrete are resistance to fragmentation of coarse aggregate, resistance to wear of coarse aggregate and resistance to polishing and abrasion of coarse aggregate to be used for surface courses, particle density and water absorption, bulk density and durability.

When required, the resistance to fragmentation of the coarse aggregates is determined in terms of the Los Angeles coefficient, according to EN 1097-2 [S-26] (Table 20.13) (ASTM C535 [S-66] and ASTM C131 [S-67]). The impact value, also determined according with EN 1097-2 [S-27], may also be required and declared as seen in Table 20.14, according to the particular application or end use.

When required, the resistance to wear of the coarse aggregates (micro-Deval coefficient, MDE) is determined according to EN 1097-1 [S-26] (Table 20.15) (ASTM D6928 [S-68]).

When required, the resistance to polishing and abrasion of the coarse aggregates to be used for surface courses is determined in terms of the following parameters: resistance to polishing (PSV), according to EN 1097-8 [S-33] (Table 20.16) (ASTM D3319 [S-69]); resistance to surface abrasion (aggregate abrasion value (AAV)), also according to EN 1097-8 [S-33] (Table 20.17); and resistance to abrasion from studded tyres (Nordic abrasion value (AN)), according to EN 1097-9 [S-34] (Table 20.18).

There are no limit requirements concerning the particle density and water absorption (determined according to EN 1097-6 [S-31]) (ASTM C127 [S-55] and ASTM C128 [S-56]) or the bulk density (determined according to EN 1097-3

Table 20.15 Categories for maximum values of resistance to impact [1]

Impact value [%]	Category SZ
≤ 18	SZ_{18}
≤ 22	SZ_{22}
≤ 26	SZ_{26}
≤ 32	SZ_{32}
>32	SZ_{Declared}
No requirement	SZ_{NR}

Table 20.16 Categories for minimum values of resistance to polishing [1]

Polished stone value	Category PSV
≥ 68	PSV_{68}
≥ 62	PSV_{62}
≥ 56	PSV_{56}
≥ 50	PSV_{50}
≥ 44	PSV_{44}
Intermediate values and those <44	PSV_{Declared}
No requirement	PSV_{NR}

Table 20.17 Categories for maximum values of resistance to surface abrasion [1]

Aggregate abrasion value	Category AAV
≤ 10	AAV_{10}
≤ 15	AAV_{15}
≤ 20	AAV_{20}
Intermediate values and those >20	AAV_{Declared}
No requirement	AAV_{NR}

Table 20.18 Categories for maximum values of resistance to abrasion from studded tyres [1]

Nordic abrasion value	Category A_N
≤ 7	A_N7
≤ 10	A_N10
≤ 14	A_N14
≤ 19	A_N19
≤ 30	A_N30
Intermediate values and those >30	A_NDeclared
No requirement	A_NNR

[S-28] (ASTM C29/C29M [S-70])) of the aggregates. The results declared on request stating the means of determination and the calculations used.

When required, the durability of the coarse aggregates is determined in terms of the following parameters: freeze-thaw resistance of coarse aggregate, according to EN 1367-1 [S-37] (Table 20.19) (ASTM C666/C666M [S-71]) or EN 1367-2 [S-38] (Table 20.20) (ASTM C88 [S-72]); volume stability, in terms of drying shrinkage, according to EN 1367-4 [S-40] (it should not exceed 0.075 %); alkali-silica reactivity (only qualitative precautions are recommended).

Table 20.19 Categories for maximum values of freeze-thaw resistance [1]

Freeze-thaw (percentage loss of mass[a])	Category F
≤ 1	F_1
≤ 2	F_2
≤ 4	F_4
>4	$F_{Declared}$
No requirement	F_{NR}

[a] In extreme situations of cold weather and/or salt or de-icing salt saturation, then tests using a salt solution or urea as detailed in EN 1367-1 may be more appropriate. The limits in this table would not apply

Table 20.20 Categories for maximum magnesium sulphate soundness [1]

Magnesium sulphate value (percentage loss of mass)	Category MS
≤ 18	MS_{18}
≤ 25	MS_{25}
≤ 35	MS_{35}
>35	$MS_{Declared}$
No requirement	MS_{NR}

Table 20.21 Categories for maximum values of acid-soluble sulphate content [1]

Aggregate	Acid-soluble sulphate content (percentage by mass)	Category AS
Aggregates other than air-cooled blast furnace slag	≤ 0.2	$AS_{0.2}$
	≤ 0.8	$AS_{0.8}$
	>0.8	$AS_{Declared}$
	No requirement	AS_{NR}
Air-cooled blast furnace slag	≤ 1.0	$AS_{1.0}$
	>1.0	$AS_{Declared}$
	No requirement	AS_{NR}

20.3.1.5 Chemical Requirements

The most relevant chemical properties of aggregates for concrete are water-soluble chloride ion content, sulphur content, other constituents' content and carbonate content of fine aggregates for concrete pavement surface courses.

When required, the water-soluble chloride ion content is determined according to EN 1744-1 [S-45] (an indicative limit of 0.01 % is provided).

When required, the sulphur content is determined in terms of the following parameters: acid-soluble sulphate content, according to EN 1744-1 [S-45] (Table 20.21); total sulphur content, also according to EN 1744-1 [S-45] (it should not exceed 2 %S by mass for air-cooled blast furnace slag and 1 %S by mass for aggregates other than air-cooled blast furnace slag; special precautions are necessary if pyrrhotite is present).

Fig. 20.8 Aggregates samples: (**a**) limestone natural aggregate; (**b**) non-crushed natural aggregate—Azores "bagacina"; (**c**) recycled aggregate

When required, the other constituents' content is determined in terms of the following parameters: content of constituents that alter the rate of setting and hardening of concrete (humus, fulvo acids, sugars), according to EN 1744-1 [S-45] (they should not increase the stiffening time of mortar test specimens by more than 120 min nor decrease the compressive strength of mortar test specimens by more than 20 % at 28 days); content of constituents which affect the volume stability of air-cooled blast furnace slag, also according to EN 1744-1 [S-45] (it should be free from dicalcium silicate disintegration and iron disintegration).

When required, the carbonate content of fine aggregates for concrete pavement surface courses is determined according to EN 196-21 [S-73] (ASTM C114 [S-74]) and EN 1744-1 [S-45] (no limits are provided).

20.3.2 Infrastructures of Transport

20.3.2.1 Scope

As previously presented, aggregates can have different origins (Fig. 20.8), such as natural material like gravel, sand or crushed rock, or they may be a by-product of an industrial process, for instance crushed slag or crushed concrete, sometimes mixed with crushed masonry and asphalt plantings and can be utilised in several structural applications such as in unbound and bounded pavement or railway track layers. The largest uses of aggregate with a structural behaviour are in pavement for highways, airfields, parking areas, storage areas and as ballast or sub-ballast layers in railways infrastructures. There are however other uses for aggregates natural and recycled or artificial, namely in pedestrian walkways, bicycles paths and other similar types of facilities [16, 17].

20.3.2.2 Unbound Granular Layers for Road and Airport Pavements: General Characteristics

The unbound granular materials are usually applied as sub-base and base layers of road and airport pavements. The sub-base of a flexible pavement is the layer constructed between the sub-grade (or the capping layer when existing) and the base layer. The base layer, or road base, is the layer underlying the bituminous layers of a flexible pavement.

The sub-base layers can be constructed from unbound granular material, or from similar bound material with a small amount of cement (between 3 % to 5 %) or other hydraulic binder. Base layers are also made from unbound crushed rock, and the aggregate can also be bounded with either cement or bitumen [18].

Although these layers are intermediary elements of the pavement structure, a proper performance of the unbound granular materials in the road pavement layers has a critical importance. These materials can be the cause of pavement failure, due to an inadequate provision of support to upper layers or by presenting insufficiently stiffness, so that they fail to transfer the load uniformly to the capping layer, leading to a localised overloading of that layer, and resulting in its rutting. As a consequence, these pavement failures may require a complete pavement reconstruction, and not only a local rehabilitation of the pavement surface where, sometimes, the problem is visible [17].

The performance of any base or sub-base layer—whether asphaltic, Portland cement concrete or unbound aggregate—relies, on the interaction of the individual particles in the mix. This stone-to-stone behaviour can be modified by the binding agent between the stone particles. For the unbound aggregate base or sub-base layers, this modification can be achieved by a combined influence of the finer aggregate particles and the water which rests in the pores of the mix. For this reason untreated aggregates can be classified as being "hydraulically" bound [19].

Due to the construction activity that usually generates large amounts of waste from different sources and processes, and to the increasing shortage of space for landfill implementation and the costs associated with waste control regulations, derived from an increasing environmental protection requirements, a most desirable alternative the natural aggregates use, and regarding the reduction of CDW volumes conducted to their reuse and recycling is needed. The incorporation of large amounts of recycled aggregates in the unbound layers of road pavements represents one of the foretold applications as it significantly contributes to a more sustainable construction and rehabilitation of road pavements [20, 21].

20.3.2.3 Unbound Granular Layers for Road and Airport Pavements: Most Important Functions

As referred, the base and sub-base layers play the most important structural function in the pavement structure, since they allow the degradation of the applied loads directly into the wearing course, contributing to reduce the stress level on the sub-grade soil to a level which the soil can withstand without major deformation (Fig. 20.9). These layers must also, in general, provide an adequate behaviour to fatigue, to crack propagation and to the action of the water [20–22].

The requirements for the base and sub-base layers are a function of the type of the road, since they also depend on the characteristics of the upper layer, namely the wearing course. Therefore different functional requirements must be considered for different types of pavements, namely for bituminous pavements, concrete pavements or block paver surfacing.

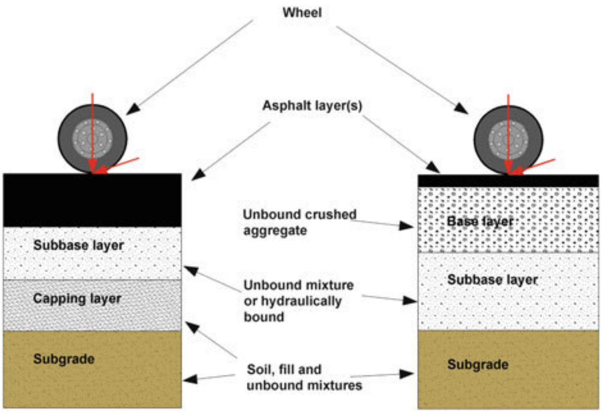

Fig. 20.9 Schematic typical flexible pavement sections (adapted from [23])

The functional requirements for base layers under asphalt pavements also depend on the thickness of the asphalt layers. When the thickness of the asphalt layer is thin, or very thin in the case of a surface treatment, the base layer is in fact the only load spreading structural layer [17]. Besides that, there are also the "unpaved roads", meaning roads where the base course is also the upper layer of the pavement, where the base layer can have different functions, such as a structural function as well as a functional function.

Therefore the unbound granular sub-base and base layers present the following main functions [16–19, 24]:

- Sub-grade protection—a structural layer which will admit greater compressive stress than the sub-grade, and thus reduces deformation of the pavement under traffic loading.
- Support the upper layer—provides an adequate support for the surfacing, since if it fails to do so the upper pavement layers will have to perform a structural role for which they are not designed.
- Construction platform—provides a stable and working platform over which the construction plant can operate when the layer above is being placed.
- Drainage—assists in reducing the water content of the sub-grade which will, in turn, help to ensure a better performance.
- Sub-grade protection against frost—when thick enough, it prevents frost form penetrating into frost-susceptible sub-grades. Countries where frost conditions are particularly severe, the insulation will be insufficient to prevent soil freezing in the winter but will help to limit differential heave by spreading the uplift effect.

Unbound granular bases may also provide a semipermeable layer, as an alternative of an entire permeable layer. For this case, they delay downward movement of contaminants from the surfacing layers. The provision of such an aggregate base will help to delay and reduce soil and groundwater pollution from pavement surface run-off.

Due to the fact that the stiffness of an unbound layer, after compaction, depends on the stiffness of the layer below it, the use of a suitable sub-base layer will raise the upper unbound base layer stiffness and will improve the bearing capacity of the pavement structure.

For the unbound pavement layers, the construction phase is a critical phase, as the partly constructed pavement is vulnerable to damage from construction traffic. During the construction of a base layer, heavy trucks carrying all the road construction materials will circulate directly on the base layer, without reduction of stresses due to the top layer [17].

20.3.2.4 Base and Sub-base Layers for Road and Airport Pavements: Applicable Technical Specifications

The specifications for the materials to be used in road and airport pavements are improving over the years and are continually being reviewed in the light of changing demands, namely due to traffic increasing.

In the case of the granular materials, the importance in the early days of road construction was on the use of locally available materials that were low cost and needed diminutive or even no processing. However, over the years specifications for unbound granular materials evolved based on experience. This empirical approach was developed as test methods originally developed for concrete aggregates and soils but later on it was also applied to specify unbound granular materials for road pavements [17, 18].

In the initial specifications for unbound pavement materials, a major importance was put on the grading of the material that covered the maximum size of aggregate and the quantity of fines. Afterwards further requirements that often are related to particle strength, such as resistance to wear and to fragmentation, resistance to frost, moisture relations, quality of fines, compaction-related parameters and shape of the material became more frequent, and presently are usually applied.

The European Standards that define the requirements for aggregates for unbound materials are:

- EN 13242—aggregates for unbound materials or treated with hydraulic binders used in civil engineering work and road construction [S-1]
- EN 13285—unbound mixtures. specifications [S-75]

The EN 13285 standard specifies the properties of aggregates and filler aggregates obtained by processing natural, manufactured or recycled materials and mixtures of these aggregates for use in hydraulically bound and unbound materials for civil engineering works. It also covers recycled aggregates with particle densities between 1.50 and 2.00 Mg/m^3. This European standard specifies requirements for unbound mixtures used for construction and maintenance of roads, airfields and other trafficked areas [S-75].

EN 13285 requires the aggregates used in unbound mixtures to comply with EN 13242, aggregates for unbound and hydraulically bound materials for use in civil engineering work and road construction [S-1]. Because EN 13242 aims to satisfy differing custom and practice across many member states of the EEA, the standard contains many choices, which are set out in tables. The structure of the tables allows the user to choose an appropriate category for each required aggregate property. EN 13242 also permits the use of the category “no requirement” for properties that are not relevant to a particular end use or origin of the mixture, in the interest of efficiency and economy. EN 13285 includes manufactured (such as slags and ashes) and recycled aggregates within its scope without specific mention in the requirement clauses. The approach adopted is blind to the source of the aggregate used in the mixture [S-1, S-75].

The scope of EN 13285 is limited to the properties of unbound mixtures at the point of delivery; it does not include water content or the properties of the finished layer. To assist in the selection of an appropriate source and to help control compaction, the system of FPC required for the unbound mixture includes an annual declaration of a typical value of laboratory dry density and optimum water content for each unbound mixture.

In Europe, and at a national level, each country can choose the requirements for aggregates, according to a detailed review of established practice and the characteristics of their aggregates, which are present at the applicable European Standards.

In Portugal, the Portuguese Road Authority [25] defined a set of technical specifications regarding the application of aggregates on base and sub-base layer that must be fulfilled.

In what concerns United States specifications for unbound sub-bases and bases, both AASHTO and ASTM have issued specifications for those materials, namely [S-76, S-77, 26]:

- AASHTO M 147—Standard Specification for Materials for Aggregate and Soil-Aggregate Sub-base, Base, and Surface Courses
- ASTM D2940—Standard Specification for Graded Aggregate Material for Bases or Sub-bases for Highways or Airports

The AASHTO specification covers the quality and grading of sand-clay mixtures; gravel, stone or slag screenings; or sand, crusher run coarse aggregate consisting of gravel, crushed stone or slag with or without soil mortar or any combination of these materials for use in the construction of sub-base, base and surface courses. The requirements are intended to cover only materials having normal or average specific gravity, absorption and gradation characteristics. Where other materials are to be used, appropriate limits suitable to their use must be specified [25, S-77].

The ASTM specification covers quality-controlled graded aggregates that, when hauled to and properly spread and compacted on a prepared grade to appropriate density standards, may be expected to provide adequate stability and load support for use as highway or airport bases or sub-bases [S-77, 26].

20.3.2.5 Unbound Aggregates for Use in Construction of Railway Track: General Characteristics

The general purpose of a railway track is to provide a safe and economical train transportation for passengers or goods. This requires the track to provide a stable guideway with an suitable vertical and horizontal alignment. In order to accomplish this role, each element of the railway track system must perform its specific functions satisfactorily in response to the traffic loads and environmental factors imposed to the system [27].

The main components of the rail track can be grouped into two categories: the superstructure and the substructure. The superstructure consists of the rails, the fastening system and the slippers (or ties). The substructure consists of the ballast, the sub-ballast and the sub-grade, being the two structures separated by the sleeper–ballast interface (Fig. 20.10).

The ballast layer is an important component of the conventional track structures. Its importance has grown by means of the increasing of axle loads and train speeds [27, 28]. Traditionally, almost all the railway lines in the world lie on a ballast layer with 200–400 mm thick. Ballast can be made of hard rocks, which are previously crushed in order to make particles of 30–50 mm size and presenting several rough edges [29], and can be constructed from different material sources like basalt, granite, slag and gravel.

The ballast structure may be divided in to four zones:

- Crib—areas defined by the sleepers
- Shoulder—it is the sloppy area between the end of the sleeper and down to the top of sub-ballast

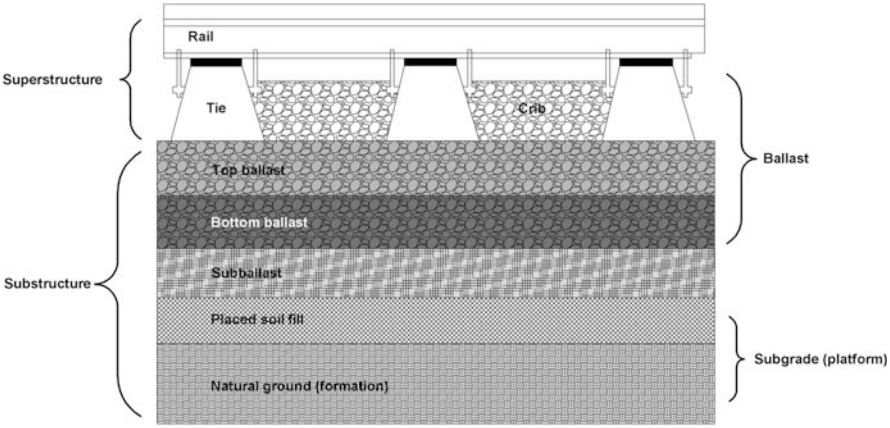

Fig. 20.10 Track structure on a longitudinal view (adapted from [27])

- Top ballast—it is the top section of the ballast structure which is usually exposed to tamping
- Bottom ballast—it is the bottom and lower part of the structure which support the overall structure

However the different types of materials such as rock aggregates, natural gravel and sand, are used according to the applied requirements, availability and cost to make ballast [29]. So, an aggregate in order to be considered as the best ballast material, must present the following properties: angularity, crushing strength and fragmentation, uniformly graded and free of dust, dirt and resistant to cementing action [27].

Depend on the quality of the sub-ballast material, loading condition, and the presence of water and drainage property of the structure; it is the more fouled part of the structure than the rest of the structure [28, 29].

20.3.2.6 Unbound Aggregates for Use in Construction of Railway Track: Most Important Functions

The ballast layer is the main structural part of railroad where the sleepers (or ties in the United States) are laid. Its main function is to transfer the loads coming from the superstructure to the sub-grade without failure, providing also a good drainage.

However, even though there are many more functions of the ballast structure, the following are usually considered as the most important functions of ballast structure [27, 28, 29]:

1. Support the actions coming from the sleepers to the substructure and retain the track in its correct position. Those actions can be grouped as uplift, lateral and longitudinal forces.
2. Pressure reducing ballast structure to the allowable stress for the underlying structure just below the sleeper.
3. Act as resiliency and energy absorbent for the track structure, namely in what concerns to noise and vibrations, specially in high speed lines;
4. The voids between the aggregates provide space for movement and accumulation of crushed aggregates due to fouling.
5. Provide quick rainwater drainage system down to the structure and contribute to the elasticity of the railway.
6. Facilitate lining operations and correction of geometry defects by the possibility of rearrange ballast particles with tamping. This eases and speeds up the maintenance operations.

Nevertheless, the flexibility of ballast layer can be also a disadvantage: under repeated train loading, the ballast particles rearrange and provoke at a long term differential track settlement. To adjust the track level, it’s necessary to tamp the ballast every time geometry goes under the intervention limits [29].

20.3.2.7 Railway Ballast: Applicable Technical Specifications

The European Standard that defines the requirements for aggregates for ballast layers is:

- EN 13450—aggregates for railway ballast [S-7]

This European Standard specifies the properties of aggregates obtained by processing natural or manufactured materials or recycled crushed unbound aggregates for use in construction of railway track. For the purposes of this standard, the aggregate is referred to as railway ballast [S-7].

In Portugal, the Portuguese Railway Authority [30] defines a set of technical specifications regarding the characterisation of aggregates for ballast. Several aggregates properties are specified in order to fulfil the applicable requirements, such as grading, resistance to wear and to fragmentation, shape and length of the material.

Regarding US specifications for aggregates for ballast, the American Railway Engineering and Maintenance-of-Way Association (AREMA), whose mission is the development and advancement of both technical and practical knowledge and recommended practices pertaining to the design, construction and maintenance of railway infrastructure, publishes a manual for railroad engineering [31] that presents, among other information, the property requirements for ballasts.

The specifications cover the types, characteristics, property requirements and manufacture of mineral aggregates for processed ballast. The type or types of processed ballast material as covered in these specifications and testing requirements shall govern the acceptance or rejection of ballast material.

Unless otherwise established by the standards of track construction and as may be defined by individual railway standards, the project design criteria, or a like document, the manual for railroad engineering shall govern the proportioning of the track substructures components [32].

Standards

[S-1] CEN—EN 13242:2013. Aggregates for unbound and hydraulically bound materials for use in civil engineering work and road construction. European Committee for Standardization (CEN), Bruxeles, http://www.cen.eu

[S-2] CEN—EN 12620:2013. Aggregates for concrete. Comité Européen de Normalisation, Brussels, Belgium

[S-3] CEN—EN 13043:2002. Aggregates for bituminous mixtures and surface treatments for roads, airfields and other trafficked areas. Comité Européen de Normalisation, Brussels, Belgium

[S-4] CEN—EN 13055-1:2002. Lightweight aggregates—part 1: lightweight aggregates for concrete, mortar and grout. Comité Européen de Normalisation, Brussels, Belgium

[S-5] CEN—EN 13139:2002. Aggregates for mortar. Comité Européen de Normalisation, Brussels, Belgium

[S-6] CEN—EN 13383-1:2002. Armourstone—part 1: specification. Comité Européen de Normalisation, Brussels, Belgium

[S-7] CEN—EN 13450:2002. Aggregates for railway ballast. Comité Européen de Normalisation, Brussels, Belgium

[S-8] CEN—EN 932-1:1996. Tests for general properties of aggregates—part 1: methods for sampling. Comité Européen de Normalisation, Brussels, Belgium

[S-9] CEN—EN 932-2:1999. Tests for general properties of aggregates—part 2: methods for reducing laboratory samples. Comité Européen de Normalisation, Brussels, Belgium

[S-10] CEN—EN 932-3:1997. Tests for general properties of aggregates—part 3: procedure and terminology for simplified petrographic description. Comité Européen de Normalisation, Brussels, Belgium

[S-11] CEN—EN 932-4. Tests for general properties of aggregates—part 4: quantitative and qualitative system for description and petrography. Comité Européen de Normalisation, Brussels, Belgium

[S-12] CEN—EN 932-5:2012. Tests for general properties of aggregates—part 5: common equipment and calibration. Comité Européen de Normalisation, Brussels, Belgium

[S-13] CEN—EN 932-6:1999. Tests for general properties of aggregates—part 6: definitions of repeatability and reproducibility. Comité Européen de Normalisation, Brussels, Belgium

[S-14] CEN—EN 932-7. Tests for general properties of aggregates—part 7: conformity criteria for test results. Comité Européen de Normalisation, Brussels, Belgium

[S-15] CEN—EN 933-1:2012. Tests for geometrical properties of aggregates—part 1: determination of particle size distribution-sieving method. Comité Européen de Normalisation, Brussels, Belgium

[S-16] CEN—EN 933-2:1995. Tests for geometrical properties of aggregates—part 2: determination of particle size distribution—test sieves, nominal size of apertures. Comité Européen de Normalisation, Brussels, Belgium

[S-17] CEN—EN 933-3:2012. Tests for geometrical properties of aggregates—part 3: determination of particle shape—Flakiness index. Comité Européen de Normalisation, Brussels, Belgium

[S-18] CEN—EN 933-4:2008. Tests for geometrical properties of aggregates—part 4: determination of particle shape—Shape index. Comité Européen de Normalisation, Brussels, Belgium

[S-19] CEN—EN 933-5:1998. Tests for geometrical properties of aggregates—part 5: determination of percentage of crushed and broken surfaces in coarse aggregate particle. Comité Européen de Normalisation, Brussels, Belgium

[S-20] CEN—EN 933-6:2014. Tests for geometrical properties of aggregates—part 6: assessment of surface characteristics—flow coefficient of aggregates. Comité Européen de Normalisation, Brussels, Belgium

[S-21] CEN—EN 933-7:1998. Tests for geometrical properties of aggregates—part 7: determination of shell content—percentage of shells in coarse aggregates. Comité Européen de Normalisation, Brussels, Belgium

[S-22] CEN—EN 933-8:2012. Tests for geometrical properties of aggregates—part 8: assessment of fines—sand equivalent test. Comité Européen de Normalisation, Brussels, Belgium

[S-23] CEN—EN 933-9:2009. Tests for geometrical properties of aggregates—part 9: assessment of fines—methylene blue test. Comité Européen de Normalisation, Brussels, Belgium

[S-24] CEN—EN 933-10:2009. Tests for geometrical properties of aggregates—part 10: assessment of fines—grading of filler aggregates (air jet sieving). Comité Européen de Normalisation, Brussels, Belgium

[S-25] CEN—EN 933-11:2009. Tests for geometrical properties of aggregates—part 11: classification test for the constituents of coarse recycled aggregate. Comité Européen de Normalisation, Brussels, Belgium

[S-26] CEN—EN 1097-1:2011. Tests for mechanical and physical properties of aggregates—part 1: determination of the resistance to wear (micro-Deval). Comité Européen de Normalisation, Brussels, Belgium

[S-27] CEN—EN 1097-2:2010. Tests for mechanical and physical properties of aggregates—part 2: methods for the determination of resistance to fragmentation. Comité Européen de Normalisation, Brussels, Belgium

[S-28] CEN—EN 1097-3:1998. Tests for mechanical and physical properties of aggregates—part 3: determination of loose bulk density and voids. Comité Européen de Normalisation, Brussels, Belgium

[S-29] CEN—EN 1097-4:2008. Tests for mechanical and physical properties of aggregates—part 4: determination of the voids of dry compacted filler. Comité Européen de Normalisation, Brussels, Belgium

[S-30] CEN—EN 1097-5:2008. Tests for mechanical and physical properties of aggregates—part 5: determination of the water content by drying in a ventilated oven. Comité Européen de Normalisation, Brussels, Belgium

[S-31] CEN—EN 1097-6:2013. Tests for mechanical and physical properties of aggregates—part 6: determination of particle density and water absorption. Comité Européen de Normalisation, Brussels, Belgium

[S-32] CEN—EN 1097-7:2008. Tests for mechanical and physical properties of aggregates—part 7: determination of the particle density of filler—pyknometer method. Comité Européen de Normalisation, Brussels, Belgium

[S-33] CEN—EN 1097-8:2009. Tests for mechanical and physical properties of aggregates—part 8: determination of the polished stone value. Comité Européen de Normalisation, Brussels, Belgium

[S-34] CEN—EN 1097-9:1998. Tests for mechanical and physical properties of aggregates—part 9: determination of the resistance to wear by abrasion from studded tyres—Nordic test. Comité Européen de Normalisation, Brussels, Belgium

[S-35] CEN—EN 1097-10:2014. Tests for mechanical and physical properties of aggregates—part 10: determination of water suction height. Comité Européen de Normalisation, Brussels, Belgium

[S-36] CEN—EN 1097-11:2013. Tests for mechanical and physical properties of aggregates—part 11: determination of compressibility and confined compressive strength of lightweight aggregates. Comité Européen de Normalisation, Brussels, Belgium

[S-37] CEN—EN 1367-1:2007. Tests for thermal and weathering properties of aggregates—part 1: determination of resistance to freezing and thawing. Comité Européen de Normalisation, Brussels, Belgium

[S-38] CEN—EN 1367-2:2009. Tests for thermal and weathering properties of aggregates—part 2: magnesium sulfate test. Comité Européen de Normalisation, Brussels, Belgium

[S-39] CEN—EN 1367-3:2001. Tests for thermal and weathering properties of aggregates—part 3: boiling test for "Sonnenbrand basalt". Comité Européen de Normalisation, Brussels, Belgium

[S-40] CEN—EN 1367-4:2008. Tests for thermal and weathering properties of aggregates—part 4: determination of drying shrinkage. Comité Européen de Normalisation, Brussels, Belgium

[S-41] CEN—EN 1367-5:2011. Tests for thermal and weathering properties of aggregates—part 5: determination of resistance to thermal shock. Comité Européen de Normalisation, Brussels, Belgium

[S-42] CEN—EN 1367-6:2008. Tests for thermal and weathering properties of aggregates—part 6: determination of resistance to freezing and thawing in the presence of salt (NaCl). Comité Européen de Normalisation, Brussels, Belgium

[S-43] CEN—EN 1367-7:2014. Tests for thermal and weathering properties of aggregates—part 7: determination of resistance to freezing and thawing of Lightweight aggregates). Comité Européen de Normalisation, Brussels, Belgium

[S-44] CEN—EN 1367-8:2014. Tests for thermal and weathering properties of aggregates—part 8: determination of resistance to disintegration of Lightweight Aggregates. Comité Européen de Normalisation, Brussels, Belgium

[S-45] CEN—EN 1744-1:2009. Tests for chemical properties of aggregates—part 1: chemical analysis. Comité Européen de Normalisation, Brussels, Belgium

[S-46] CEN—EN 1744-3:2002. Tests for chemical properties of aggregates–part 3: preparation of eluates by leaching of aggregates. Comité Européen de Normalisation, Brussels, Belgium

[S-47] CEN—EN 1744-4:2005. Tests for chemical properties of aggregates—part 4: determination of water susceptibility of fillers for bituminous mixtures. Comité Européen de Normalisation, Brussels, Belgium

[S-48] CEN—EN 1744-5:2006. Tests for chemical properties of aggregates—part 5: determination of acid soluble chloride salts. Comité Européen de Normalisation, Brussels, Belgium

[S-49] CEN—EN 1744-6:2006. Tests for chemical properties of aggregates—part 6: determination of the influence of recycled aggregate extract on the initial setting time of cement. Comité Européen de Normalisation, Brussels, Belgium

[S-50] CEN—EN 1744-7:2012. Tests for chemical properties of aggregates—part 7: determination of loss of ignition of Municipal Incinerator Bottom Ash

Aggregate (MIBA Aggregate). Comité Européen de Normalisation, Brussels, Belgium

[S-51] CEN—EN 1744-8:2012. Tests for chemical properties of aggregates—part 8: sorting test to determine metal content of Municipal Incinerator Bottom Ash (MIBA) Aggregates. Comité Européen de Normalisation, Brussels, Belgium

[S-52] CEN—FprEN 16236:2011. Evaluation of conformity of aggregates (final draft). Comité Européen de Normalisation, Brussels, Belgium

[S-53] ASTM—C33/C33M (2013) Standard specification for concrete aggregates. American Society for Testing and Materials, West Conshohocken, PA

[S-54] ASTM—C295/295M (2012) Standard guide for petrographic examination of aggregates for concrete. American Society for Testing and Materials, West Conshohocken, PA

[S-55] ASTM—C127 (2012) Standard test method for density, relative density (specific gravity), and absorption of coarse aggregate. American Society for Testing and Materials, West Conshohocken, PA

[S-56] ASTM—C128 (2012) Standard test method for density, relative density (specific gravity), and absorption of fine aggregate. American Society for Testing and Materials, West Conshohocken, PA

[S-57] ASTM—C136. Test method for sieve analysis of fine and coarse aggregates. American Society for Testing and Materials, West Conshohocken, PA

[S-58] ASTM—C330/C330M (2013) Standard specification for lightweight aggregates for structural concrete. American Society for Testing and Materials, West Conshohocken, PA

[S-59] ISO 565:1990 (1990) Test sieves—metal wire cloth, perforated metal plate and electroformed sheet—nominal sizes of openings. International Standardization Organization, Geneva, Switzerland

[S-60] ASTM—D4791 (2010) Standard test method for flat particles, elongated particles, or flat and elongated particles in coarse aggregate. American Society for Testing and Materials, West Conshohocken, PA

[S-61] ASTM—D3398 (2006) Standard test method for index of aggregate particle shape and texture. American Society for Testing and Materials, West Conshohocken, PA

[S-62] ASTM—C136 (2006) Test method for sieve analysis of fine and coarse aggregates. American Society for Testing and Materials, West Conshohocken, PA

[S-63] ASTM—D2419 (2009) Test method for sand equivalent value of soils and fine aggregate. American Society for Testing and Materials, West Conshohocken, PA

[S-64] AASHTO—T330 (2007) Method of test for the qualitative detection of harmful clays of the smectite group in aggregates using methylene blue. American Association of State Highway and Transportation Officials, Washington, DC

[S-65] ASTM—C1777 (2013) Standard test method for rapid determination of the methylene blue value for fine aggregate or mineral filler using a colorimeter. American Society for Testing and Materials, West Conshohocken, PA

[S-66] ASTM—C535 (2012) Test method for resistance to degradation of large-size coarse aggregate by abrasion and impact in the Los Angeles machine. American Society for Testing and Materials, West Conshohocken, PA

[S-67] ASTM—C131 (2006) Test method for resistance to degradation of small-size coarse aggregate by abrasion and impact in the Los Angeles machine. American Society for Testing and Materials, West Conshohocken, PA

[S-68] ASTM—D6928 (2010) Standard test method for resistance of coarse aggregate to degradation by abrasion in the micro-Deval apparatus. American Society for Testing and Materials, West Conshohocken, PA

[S-69] ASTM—D3319 (2011) Standard test method for accelerated polishing of aggregates using the British wheel. American Society for Testing and Materials, West Conshohocken, PA

[S-70] ASTM—C29/C29M (2009) Test method for bulk density ("unit weight") and voids in aggregate. American Society for Testing and Materials, West Conshohocken, PA

[S-71] ASTM—C666/C666M (2008) Test method for resistance of concrete to rapid freezing and thawing. American Society for Testing and Materials, West Conshohocken, PA

[S-72] ASTM—C88 (2013) Test method for soundness of aggregates by use of sodium sulfate or magnesium sulfate. American Society for Testing and Materials, West Conshohocken, PA

[S-73] CEN—EN 196-21:2005. Methods of testing cement—part 21: determination of the chloride, carbon dioxide and alkali content of cement. Comité Européen de Normalisation, Brussels, Belgium

[S-74] ASTM—C114 (2013) Standard test methods for chemical analysis of hydraulic cement. American Society for Testing and Materials, West Conshohocken, PA

[S-75] CEN—EN 13285:2010. Unbound mixtures—specification. Comité Européen de Normalisation, Brussels, Belgium

[S-76] AASHTO M147 (2013) Standard specification for materials for aggregate and soil-aggregate sub base, base, and surface courses. AASHTO American Association of State Highway and Transportation Officials, Washington, DC. http://www.transportation.org

[S-77] ASTM—D2940 (2009) Standard specification for graded aggregate material for bases or subbases for highways or airports. American Society for Testing and Materials, West Conshohocken, PA

Books/Magazines/Journals

Cement and Concrete Composites
Cement and Concrete Research
Cement, Concrete and Aggregates
Construction and Building Materials
International Journal of Pavement Engineering

Journal of Advanced Concrete Technology
Magazine of Concrete Research
Materials and Structures
Road Materials and Pavement Design

Associations/Organisations/Societies

- Comité Européen de Normalisation—https://www.cen.eu/Pages/default.aspx
- American Society for Testing and Materials—http://www.astm.org/ABOUT/aboutASTM.html

Companies

- Aggregate Industries—http://www.aggregate.com/
- Brett Aggregates—http://www.brett.co.uk/aggregates
- Compagnie des Agrégats du Sud en SA—http://www.salespider.com/bw-5785827/compagnie-des-agregats-du-sud
- Cimpor Cimentos de Portugal, Agregados—http://www.cimpor.pt/

References

1. Duran J (2000) Sands, powders and grains. Springer, New York, NY
2. Jaeger HM, Nagel SR, Behringer RP (1966) The physics of granular materials. Phys Today 49:32–38
3. Antony SJ, Hoyle W, Ding Y (eds) (2004) Granular materials, fundamentals & applications. The Royal Society of Chemistry, Cambridge
4. Atkins HN (1980) Highway materials, soils, and concretes, 3rd edn. Prentice Hall, Englewoods Cliff, NJ
5. Ivanov Y, Cheskov V, Natova M (2001) Polymer composite materials interface phenomena & processes. Kluwer, Dordrecht
6. Mehta A (2007) Granular physics. Cambridge University Press, Cambridge, UK
7. Rao KK, Nott BR (2010) An introduction to granular flow. Cambridge University Press, Cambridge
8. Wu A, Sun Y (2008) Granular dynamic theory & applications. Springer, Berlin
9. Tejchman J (2013) Confined granular flow in silos. Springer, Dordrecht
10. da Vinci L (1495) Codex Madrid 1
11. Amontons G (1699) Histoire de l'Académie Royale des Sciences avec les Mémoires de Mathématique et de Physique, p 206
12. Coulomb CA (1779) Théorie des Machines Simples, en Ayant Égard au Frottement de Leurs Parties et à la Roideur des Cordages
13. Barrat JL, Feigelman MV, Kurchan J, Dalibard J (eds) (2002) Slow relaxations & nonequilibrium dynamics in condensed matter. Springer, Berlin
14. Mitarai N, Nori F (2006) Wet granular materials. Adv Phys 55:1–45
15. Song Y, Yongjun C (2012) Study on dynamic contact angles and capillary forces between two spherical particles. In: Proceedings of international conference on mechanical engineering and material science (MEMS 2012). Atlantis Press, Paris

16. National Stone Association (1993) The aggregates handbook. Editor Richard D. Barksdale, Washington, DC
17. COST 337 (1999) Unbound granular materials for road pavements. Final report on cost action 337
18. Croney D, Croney P (1997) Design and performance of road pavements, 3rd edn. McGraw Hill, London
19. Dawson AR (1995) The unbound granular base. Keynote paper. In: Center for Aggregates Research, third annual symposium, Austin, Texas
20. Freire AC, Neves J, Pestana R (2009) Analysis of recycled aggregates properties for unbound granular asphalt pavement layers. In: Proceedings of the 11th conference on Asphalt Pavements, Nagoya, Japan
21. Freire AC, Neves J, Roque AJ, Martins IM, Antunes ML, Faria G (2011) Sustainable application of construction and demolition recycled materials (C&DRM) in road infrastructure. In: Proceedings of the first international conference on WASTES: solutions, treatments and opportunities, Guimarães, Portugal
22. Neves J (2001) Contribuição para a modelação do comportamento estrutural de pavimentos rodoviários flexíveis. Tese de doutoramento para obtenção do grau de Doutor em Engenharia civil, Instituto Superior Técnico (in Portuguese)
23. Araya AA (2011) Characterization of unbound granular materials for pavements. Master of Science in Transport and Road Engineering, IHE/TUDelft, The Netherlands
24. Freire AC (1995) Estudos relativos a camadas de pavimentos constituídas por materiais granulares. Dissertação de Mestrado, Universidade Nova de Lisboa (in Portuguese)
25. EP (2009) Caderno de encargos—tipo obra, Estradas de Portugal, I.P. (in Portuguese)
26. AASHTO (1993) Guide for the design of pavement structures. American Association of State Highway and Transportation Officials, Washington, DC, http://www.transportation.org
27. Selig ET, Waters JM (1994) Track geotechnology and substructure management. Thomas Telford Publications, London
28. Mundrey JS (2009) Railway track engineering (4th edn). Tata McGraw Hill, New Delhi
29. Paderno C (2009) Simulation of ballast behaviour under traffic and tamping process. In: LAVOC—EPFL. Conference paper STRC 2009
30. REFER (2008) IT.GEO.001—Fornecimento de Balastro e Gravilha, versão 03, REFER, Rede Ferroviária Nacional E.P. (in Portuguese)
31. AREMA (2010) AREMA manual for railway engineering. American Railway Engineering and Maintenance-of-Way Association, Lanham-Seabrook
32. RailAmerica Engineering (2011) Industrial track construction specifications, U.S.A.

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M.C. Gonçalves, F. Margarido (eds.), *Materials for Construction and Civil Engineering*, DOI 10.1007/978-3-319-08236-3