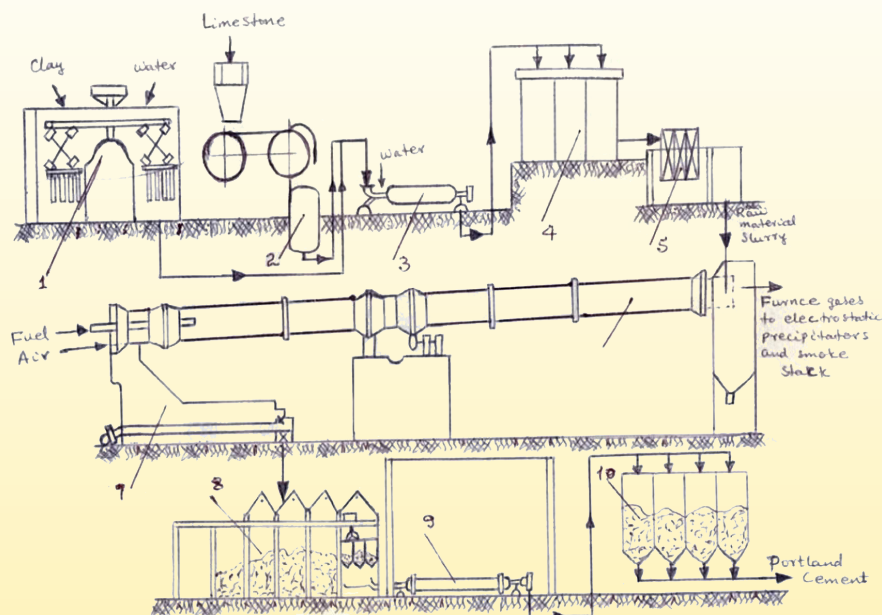




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Concise Introduction to Cement Chemistry and Manufacturing



Tadele Assefa Aragaw

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Concise Introduction to Cement Chemistry and Manufacturing

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Bahir Dar University, Ethiopia

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ABSTRACT

This book is designed to be used in an introductory sophomore-level undergraduate course in chemical engineering, civil engineering, industrial engineering, chemistry, and/or industrial chemistry. Senior-level students in resource development, soil science, and geology might also find this book useful. In addition, it is our hope that even advanced mathematics-oriented high school seniors might find the material easy to master as well.

This book emphasizes concepts, definitions, chemical equations, and descriptions with which some chemical science professionals struggle. It stresses the importance of maintaining uniformly high standards in pure chemical science and manufacturing technology while still keeping in mind that procedures that might seem strange also yield results that prove effective.

KEYWORDS

cement chemistry, cement production, clinkerization, dry process, manufacturing, Portland cement, wet process

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Preface

This book deals with the chemistry of the principal silicate and aluminate cements used in building and civil engineering. Emphasis is placed throughout on the underlying science and manufacturing process but detail practical applications which are well covered in other works.

In order to help the readers understand the context in which this book has been dartered for chemical engineering, civil engineering, industrial chemistry, chemistry, soil science, and geology disciplines, the book represents a summary information collected from limited number of sources and written by the author's understanding the science behind cement chemistry and manufacturing. The information provided in this book is intended to be used as an input to the determinations of the principles of production and chemistry of cement in specific areas.

The rest of this section describes the type of information that is provided in each chapter of the book.

Chapters 1, 2, and 3 provide general information on cement production in the world, together with its marketing, classification, and type of cements, chemistry, and raw material, the formation of limestone, additives, and pozzolan materials in cement processing.

Chapters 4, 5, 6, and 7 describe in more detail the mining of raw materials and composition; clinkerization and production processes of cement including the advantages and disadvantages of the dry and wet production mechanisms with quality and economic aspect; its burnability.

Chapters 8, 9, 10, and 11 present the testing of the produced cement materials with certain parameters; hydration effects of Portland cement for the cement strength; different types of cement and storage mechanisms.

Chapter 12 describes the technical analysis of basic cement quality parameters with a detailed laboratory procedure.

It is therefore of the utmost importance that the information contained in this book is fully take into account the best available techniques that change over time. This book will be reviewed and updated as appropriate.

Tadele Assefa Aragaw
April 2018

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Tadele Assefa Aragaw
April 2018

CHAPTER 1

Introduction

World cement [3] production has registered more than a nine-fold increase over the last three and a half decades—from 133 million tons in 1950 to 860 million tons in 1979 to 1 billion tons in 1985. At the same time, there has been tremendous technological progress in the cement manufacturing process, which is being continuously updated through the introduction of new technological advances for capacity enhancement as well as by various devices for energy economy and conservation. Such developments during the past few decades have inevitably imposed greater responsibility on the geologists and mining engineers engaged in exploration and exploitation of raw materials for cement manufacture.

Cement is the name given to mineral powders which when mixed with water form a plastic body that easily can be shaped and that hardens after some time to yield a strong, stone hard body. Cement is used for making building and plastering mixes (lime), structural and decorative articles (Plaster of Paris and magnesia cements), prefabricated concrete and reinforced concrete structural items, underground and hydraulic structures, etc. As can be understood from the uses, the production of cement in a country, particularly a developing one such as Ethiopia, has to be given great importance.

1.1 CLASSIFICATION OF CEMENTS

Depending on their uses and properties, cements are divided into three main groups.

1. Air cements: harden and retain their strength in air. They include: air lime, gypsum, and magnesium cements. These materials are used for making buildings and plastering (lime) and structural and decorative articles (Plaster of Paris and magnesia cements).
2. Hydraulic cements: harden and retain their strength in water. They include: hydraulic lime, Roman cement, Portland cement, and cement with various admixtures (Pozzolan cement, Portland slag cement), alumina cements, etc. Hydraulic cements are more important than air cements and are used for making prefabricated concrete and reinforced-concrete structural items and parts of buildings as well as underground and hydraulic structures.
3. Acid-resistant cements: hardening withstands the action of mineral acids such as H_2SO_4 , HNO_3 , HCl , etc.

In building practices, cements are used in the form of structural pastes of several types: grouts (i.e., a mixture of cement with water, mortars, mixtures of cement with water and fine ag-

2 1. INTRODUCTION

gregate (sand)), and concrete mix containing cement, water fine, and coarse aggregate (cement, gravel, crushed stone).

The hardened mix is called concrete, and concrete embedded with steel is known as reinforced concrete.

CHAPTER 2

Raw Materials and Their Components for Cement Production

The raw materials for making cement are naturally occurring materials as well as some industrial waste products. The naturally occurring materials include: gypsum minerals (gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, anhydrite CaSO_4), limestone minerals (limestone, chalk, dolomites), and clay minerals (clays and marbles, silica sand, bauxites). The industrial waste minerals used for making cements include: metallurgical slag, the nepheline sludge of the alumina manufacturing industry, and the sodium hydroxide production sludge, which contains CaCO_3 , pyrite cinder, etc.

The raw-meal feed for cement making basically contains four types of compounds: carbonates aluminosilicates, iron components, aluminum compounds (oxide), and minor constituents. Out of these, the first three are very important in the formation of cement clinker, while the fourth affects the manufacturing process (mainly burning, stabilization of the kiln, and pre-heated performance) depending upon the type and quantity of the minor constituents present. The three main components should satisfy among themselves the compositional compatibility, thermal combinability, and physical amenability (responsibility) to production processes (crashing, grinding and homogenization, burning and clinker formation).

2.1 THE RAW MATERIAL COMPONENTS

The calcareous component of the cement raw meal is usually any rock containing CaCO_3 . Limestone is the most commonly available calcium carbonate rock. Besides CaCO_3 present as calcite or aragonite, these rocks also contain various quantities of impurities like: quartz, clay, phosphates, opal (SiO_2), pyrite (FeS_2), siderite (FeCO_3), goethite ($\text{FeO} \cdot \text{OH}$), dolomite ($\text{CaMg}(\text{CO}_3)_2$), magnetite, gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), fluorite (CaF_2), bituminous impurities, etc.

The type of limestone is characteristic of its mode of origin and has definite implication for cement making as well as for various production processes. The mode of origin has also profound effects on the mineral form, degree of crystalline, grain size, cementing medium, degree of compaction, mode, and mineral form of occurrence of the impurities in the limestone and controls its physical, technological, dissociation, and combinability properties. Each of these properties has

4 2. RAW MATERIALS AND THEIR COMPONENTS FOR CEMENT PRODUCTION

significant bearing in the process control and optimization in cement manufacture. The mode of origin controls the association of various rocks, found interbedded, or as intercalations (anything out of ordinary course), gradations, or impurities in limestone.

Study of this factor is important for regional prospecting and delineation of the rock types. The environments of deposition control the chemical (major and minor constituents) composition and their variations account for the direct suitability of the rock. The details of the physico-chemical environment and its variations control the mineralogical composition, degree of crystallinity, grain size, nature, and extent of cementing material in the rock. The first three factors primarily control the reactivity and thermal combinability of the fine raw meal obtained from the rock, while the last three control the amenability of the rock to fine grinding for raw meal preparation. At the same time, the reactivity and burnability of a raw meal depends upon its fineness.

Present-day cement manufacture in large plants is based on the advanced technology of process optimization in which energy conservation is the main constituting factor. Fuel used for raw-material burning and electrical energy used for crushing, grinding, and homogenization, also primarily based on fuel as source, can be effectively conserved through a proper understanding of the behavior of the raw materials to size reduction and burning processes.

It is therefore apparent that a knowledge about the different modes of formation of limestones, the geological and structural peculiarities, and the lithological association with different other rock types is therefore an essential prerequisite for regional prospecting and exploration for selecting an appropriate deposit while detailed study of the mineralogical association, textural, structural, and granulometric characteristics of the deposit is essential to understand and control its behavioral pattern in cement manufacture.

2.2 MODE OF FORMATION OF LIMESTONES

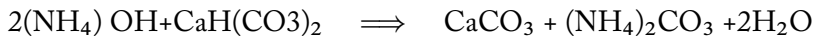
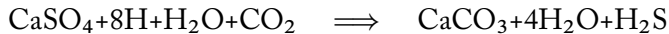
Wide compositional, textural, and granulometric variations among limestones and their frequent intimate associations with clays, dolomites, and other rock types reflect their varied mode of formation. A brief appraisal of different environments and physical-chemical factors controlling carbonate formation is helpful in limestone prospecting as well as in their quality evaluation. Carbonate rocks are mainly the products of deposition in shallower marine environments.

1. Mechanism and Process of Formation

The majority of carbonates is of sedimentary origin and is formed by:

- (a) crystallization of calcium carbonate as an initial solid material by both organic and inorganic precipitation or by a combination of both;
- (b) chemical and/or mechanical breakdown of pre-existing rocks, transportation of the products either as detrital particles or in chemical solution, and the deposition or precipitation in standing bodies of water in a layered sequence;

- (c) lithification of calcium carbonate sediments under low-temperature, low-pressure conditions which include various steps beginning with the change of grain mineralogy, addition of coatings to grains, selective dissolution of matrix and/or grains, precipitation of mineral cement in pores, recrystallization, etc.; and
- (d) replacement of calcium sulphate or quartz by calcium carbonate under the effect of sulphate reducing bacteria, by ammonification or nitrate reduction. This is a less common process.



2. Chemical Precipitates

These may be biogenic or inorganically precipitated rocks. The deposits may be well-bedded, thick, and uniform and may have aphanitic, cryptocrystalline, or fine-grained granulometry. The rocks are usually dense with low porosity and extensively uniform laminations.

3. Detrital Carbonates

These consist of gravel, sand, or clay-sized fragments derived from other carbonate rocks. The detrital fragments constituting the framework are cemented by normal precipitates, which may be microcrystalline calcite (micrite) or sparry calcite cement (sprite) and other post-depositional replacement or recrystallization minerals. Such limestones are usually hard, compact, and show high compressive strength and difficult grindability.

2.3 CARBONATE ASSOCIATIONS

Calcium occupies a unique position in its ionic radius (0.99 Å) which is intermediate between small and large cations. It can form either rhombohedra (calcite) or orthorhombic (aragonite) carbonates. Other calcite-type rhombohedra carbonates include MgCO_3 , and FeCO_3 . Aragonite type includes SrCO_3 , BaCO_3 , and PbCO_3 . Iron-containing carbonates dissociate at lower temperatures and are comparatively more reactive than pure or siliceous limestones. Aragonite-type minerals show preferential substitution with larger cations, while surface conditions, calcite, aragonite, and dolomite are the common carbonate minerals.

Additives and Corrective Materials in Cement Production

Additives are naturally occurring rocks or industrial wastes which are added to a raw mix to compensate its compositional deficiency for cement making or to correct marginal deviations from the desired composition. For a very pure limestone, additives may be generally distinguished as argillaceous components and corrective materials are ferruginous components. The role of either may be reversible, significant, or minor depending upon the compositional characteristics of the limestone.

Various admixtures are introduced to the cements to give them the required properties and also to reduce manufacturing costs. Hydraulic admixtures: containing alumina, which increase the resistance of cements to the effects of water and aid hardening under water; plasticizing agents: surface-active substances which increase the elasticity and bonding properties of the cement paste: Inert aggregates (sand, limestone, dolomite), acid-resistant admixtures (andesite, beschfaunite, granite), etc.

Besides chemical composition, one important aspect in the choice of additives and corrective materials with respect to a particular limestone is the compatibility among their physical, mineralogical, and thermal combinability characteristics, which control, respectively, effective grinding and homogenization, dissociation, and clinkerization.

Exploration of Raw Materials for Cement Manufacturing

4.1 SIGNIFICANCE OF RAW MATERIALS EXPLORATION IN CEMENT MAKING

1. Large limestone deposits need be prospected for increasingly larger capacity of individual plants.
2. Depletion of large, good-quality, and favorably located deposits through exploitation necessitated falling back upon inferior-grade and less favorably accessible deposits.
3. More rigid implementation of statutory regulations on noise and dust control excludes use of many good deposits located near habitations.
4. Higher capital investment on cement plants because of both rising costs and higher capacity installations intensifies the need for greater reliability in raw material proving to minimize the entrepreneurial risk.
5. The increasingly rigorous demands on better cement quality impose more rigid requirements on raw material quality.
6. The rapid switch-over to the energy-saving dry process of cement manufacture with suspension preheaters calls for:
 - (a) thorough homogenization or raw meal for better reactivity, where compatibility of physical and technological properties of the raw meal constituents is a primary prerequisite, and
 - (b) a lesser permissible limit for deleterious minor constituents in raw materials and cement.

4.2 OBJECTIVES OF EXPLORATION

1. Location of cement plant, taking into consideration the principal factors, i.e., location of the raw-material deposits, availability of infrastructural facilities, such as power, transport and communication, and nearness to the marketing region.

10 4. EXPLORATION OF RAW MATERIALS FOR CEMENT MANUFACTURING

2. Optimum size and working life of a plant based on raw material availability; market conditions guided by the scope and extent of capital investment and the risk factor involved.
3. Choice of manufacturing process. Dry, semi-dry, or wet process of manufacture, depending upon moisture content, minor constituents present in raw material, cost and availability of solid (coal), liquid (oil products), and gaseous fuels.
4. Quality of the product and scope of manufacture of different types of cement. The quality of raw materials controls that of clinker, its specific quality characteristics and availability of other subordinate raw materials, or industrial wastes defines the scope of manufacturing ordinary Portland cement, white cement, Portland pozzolana cement, etc.
5. System design in the cement manufacturing process. The crushability and grindability of limestone and the raw mix components decides the types of crushers and mills; the degree of uniformity inequality or raw material deposits dictates the need or otherwise for pre-blending or homogenization installations; and the type and quality of harmful minor constituents decides the design of the preheater and the extent of bypass of kiln exit gases.
6. Mine planning and quarry layout. The geographic geologic characteristics of the raw-material deposit, such as terrain condition, over burden, mode of occurrence, and structural features determine the mine layout, the number and height of benches, direction of mining and scope of selective quarrying for uniform mine output, etc.; the lithologic, i.e., textural, structural, and fracturing (strength) properties of the rock decides upon the choice of mining method, by drilling and blasting or ripping. The quarry layout, distance from plant, and topography of the region decide the choice of loading and transport machineries, their number and capacity, i.e., shovels, excavators, dragline, etc., for transport to the crusher or plant.

The Composition of Portland Cement and Production Process

Portland cement was first introduced in 1824 by Joseph Aspdin, a brick layer from Leeds, England [5]. On setting, the color of cement resembles the color of rocks near Portland, England, hence the name.

Approximate composition of raw material used for manufacturing ordinary Portland cement is: clinker (percent by weight) varies within the limits shown in Table 5.1.

Table 5.1: Chemical compositions of cement

Calcium Oxide (CaO)	60–65%
Silica (SiO ₂)	20–25%
Aluminum Oxide (Al ₂ O ₃)	4–8%
Ferrous Oxide (Fe ₂ O ₃)	2–4%
Magnesium Oxide (MgO)	1–3%

All the above compounds undergo some chemical combinations during the process of burning and fusion. Main constituents of cement are: 3CaO.SiO₂, 2CaO.SiO₂, 3CaO.Al₂O₃. Tri-calcium silicate is the best cementing material and the more it is present in cement the better the cement is. In a properly burnt clinker, 3CaO.SiO₂ should be about 40%. In a properly burnt clinker it shall have less of 3CaO.SiO₂ and more of free lime.

After the addition of water to cement it sets and hardens due to the hydration and hydrolysis of the above three compounds which act as a glue. The aluminates are the first to set and harden. Trisilicate is slower, and disilicate is the slowest. As such, the initial setting of cement is due to Trisilicate. Disilicate takes 14–18 days to add the strength. All three compounds in their action with water give out heat. Maximum heat giving compound is the aluminates which is responsible for most of the undesirable properties of concrete. Cement having lesser aluminates shall have less initial strength but higher intimate strength. Also, there will be less generation of heat, more volumetric stability, less cracking, and more resistance to acid attacks. Incomplete

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burning of clinker leaves free lime in it. This free lime causes expansion and disruption of concrete after use. The silicates form a gel with water. The gel fills the pores of cement there by making it impervious. The gel later on crystallizes and firmly binds the particles.

According to IS 269-1975, composition of ordinary Portland cement shall satisfy the following conditions.

1. Ratio of the percentage of lime to that of silica, alumina, and iron oxide when calculated by the formula

$$\frac{\text{CaO} - 0.75\text{O}_3}{2.8\text{SiO}_2 + 1.2\text{Al}_2\text{O}_3 + 0.65\text{Fe}_2\text{O}_3}$$

shall not be less than 0.66 and not more than 1.02.

2. Ratio of percentage of alumina to that of iron oxide shall not be less than 0.66.
3. Weight of insoluble residue shall not be less than 2%.
4. Weight of magnesia shall not be more than 6%.
5. Total sulphur contents calculated as SO_3 (sulphuric anhydride) shall not be more than 2.75%.
6. Total loss on ignition shall not be more than 4%.

In commercial practice the charge composition is calculated on the basis of the required percentage ratio of the basic oxides in the clinker. These ratios are called modules, the silicate module “n” and the alumina module “p”:

$$n = \frac{\% \text{SiO}_2}{\% \text{Al}_2\text{O}_3 + \% \text{Fe}_2\text{O}_3}$$

$$p = \frac{\% \text{Al}_2\text{O}_3}{\% \text{Fe}_2\text{O}_3}$$

$$KS = \frac{(\text{CaO overall} - \text{CaO free}) - (1.65\text{Al}_2\text{O}_3 + 0.35\text{Fe}_2\text{O}_3 + 0.7\text{SO}_3)}{2.8(\text{SiO}_2 \text{ overall} - \text{SiO}_2 \text{ free})}$$

The basic characteristics describing the mineral composition of Portland cement clinker is the coefficient of saturation of the silica with lime, *KS*, expressing the ratio of the amount of lime remaining in the clinker after formation of $2\text{CaO} \cdot \text{SiO}_2$, $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, and CaSO_4 to the amount of lime necessary for combining with the silica to form $3\text{CaO} \cdot \text{SiO}_2$.

Using given values of modules and *KS* and also data obtained by chemical analysis of the raw materials, limestone, and clay, their ratio by weight in the charge is computed. For Portland cement the coefficient of saturation lies between 0.8 and 0.95. The lower the *KS* value, the higher the content of $2\text{CaO} \cdot \text{SiO}_2$ in the clinker and lower the activity of the cement.

In the manufacturing of Portland cements the properties of the final products owe their origin to clinker and gypsum and other additives that are introduced during the process of grinding, and changes that place during the process of grinding and subsequent storage. Any consideration of the characteristics of raw materials requires a basic understanding of the factors that control the clinker quality and the clinkerization process.

5.1 CLINKERIZATION PROCESS

5.1.1 CLINKER CHARACTERISTICS

The clinker characteristics that are significant in achieving a quality product can be summarized as follows:

1. appropriate bulk chemical composition;
2. formation of hydraulically active phases;
3. optimum grain growth;
4. optimum proportion of different phases; and
5. proper microstructural development.

A quality clinker can be produced if the following measures are adopted.

1. Achieving the bulk chemical composition of clinker in the following range:

CaO (C)	63–67%
Al ₂ O (A)	4–7%
Fe ₂ O ₃ (F)	2.4%
SiO ₂ (S)	21–24%

$$C + A + F + S = 98-93 \text{ to } 93-91$$

$$\text{MgO} + \text{K}_2\text{O} + \text{SO}_3 + \text{P}_2\text{OS} + \text{TiO}_2 = 2-3 \text{ to } 7-9\%$$

2. Stabilizing the hydraulically active clinker phases including the high-temperature polymorphic forms of alite (Ca₃SiO₃) and belite (B-Ca₂SiO₄).
3. Optimizing the proportions of the major phases in a clinker, where the alite content should be aimed as high as possible, preferably in the range of 55–65%, and aluminates and ferrite phase in the range 9–11% and 12%, respectively, the balance being made up of belite.
4. Keeping the average grain size of the clinker minerals around 30 μm and raising the maximum crystal size of alite grains even higher to the extent possible but not exceeding the range 70–100 μm.

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- 5. Forming monodblastic texture, i.e., a microstructure in which there is little clustering of grains with alite and belite crystals being well distributed over the entire clinker volume as independent grains having well-crystallized aluminates and ferrite phase in the interstices.

5.1.2 CLINKERIZATION PHENOMENON VIS-À-VIS CLINKER CHARACTERISTICS

It is well known that the above measures adopted to achieve clinker quality are realized through the clinkerization process which can be represented in a simplified form by the reaction steps given in Fig. 5.1.

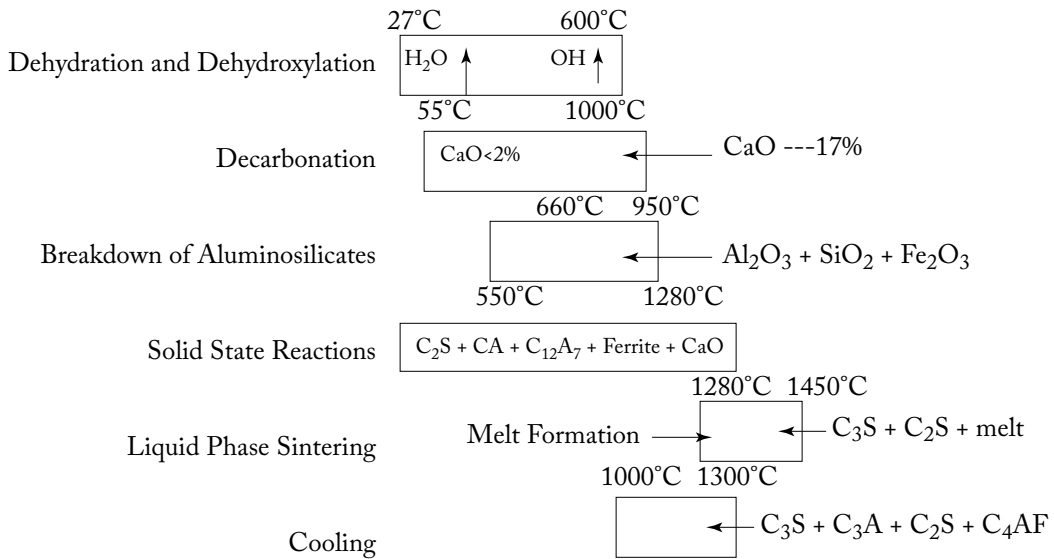


Figure 5.1: Approximate reaction sequence in clinkerization.

It is evident from this summary diagram that the clinkerization phenomenon is strongly dependent on the reactivity (signifying the achievable rate of different reactions at respective temperature within practical time limits) and burnability (signifying the overall measure of ease or difficulty of burning under practical operating conditions) or raw mixes, which, in turn, depend on the intrinsic characteristics of the constituent raw materials. In this context it should be kept in mind that the burning process (Fig. 5.2) has several interdependent and interrelated controlling factors, which means that knowledge of the raw material characteristics is necessary to match the need of systems design and operation.

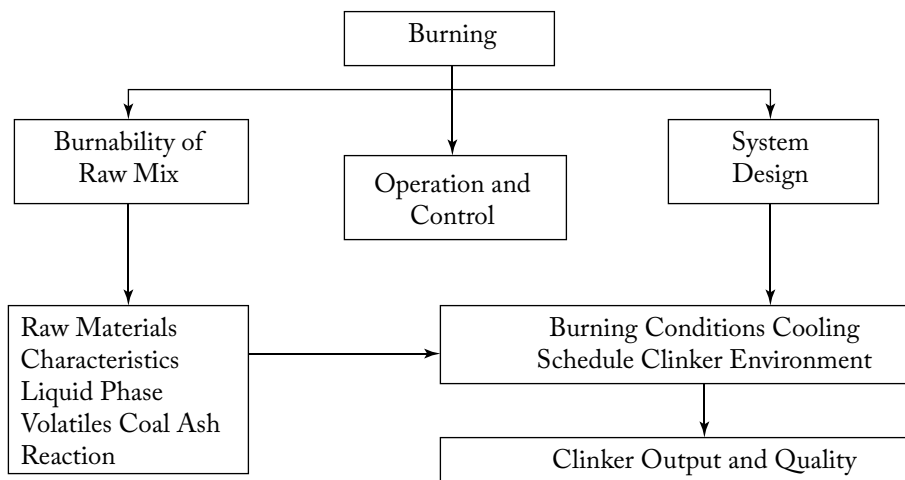


Figure 5.2: Major factors controlling the burning operations.

5.2 RAW MATERIALS FOR CEMENT MAKING

The common raw materials for cement making have been classified and categorized in Tables 5.2 and 5.3. It is well known that the dispersed raw meal feed for cement manufacture basically consists of two components—calcium carbonate and aluminosilicates—that are complementary in nature.

Table 5.2: Raw materials in combined methods of manufacture of cement

Principal raw material	Source	Products
Blast-furnace slag	Blast furnace of iron and steel industry	Clinker, slag cement, road ballast slag wool, slag bricks, lightweight aggregate
Calcium sulphate	Natural gypsum chemical gypsum	Cement sulphuric acid
Calcium silicate	Nepheline waste	Cement, alumina, fertilizers
Salt brine and limestone	Soda manufacturing industry	Caw tic soda, white cement
Dolomite	Natural	Cement, magnesia
Cement raw materials and rhyolitic tuff rocks	Natural	Cement, fertilizers

Table 5.3: Raw materials for Portland cement industry

Category	Nature	Materials in use
Materials for Clinker Production		
Principal	Carbonates	Limestone, chalk, marble, sea shell, moral, carbonate sludge of paper, sugar, and fertilizer industries
	Aluminosilicates	Clay, soil, shale, phyllites, slate, and volcanic rocks. Fly ash from thermal power stations
	Lime-silicates	Wollaston tic rocks, metallurgical silages, wastes of aluminum industry
Supplementary	Corrective materials	Sand and sandstones, buxite, iron are laterite, pyrite cinders from chemical industry
Special Additives	Grinding acids, etc.	Surface active agents like triethnolamine sulphate lye, sodium paly phosphate, etc.
	Slurry thinners, etc.	Surface active agents
	Granulation Activators Mineralizes	Chemical reagents like Na_2CO_3 , CaF_2 , Na_2SiF_6 , $\text{Ca}_3(\text{PO}_4)_3$, CaSO_4 , $2\text{H}_2\text{O}$, etc.
Materials for Converting Clinker into Cement		
Principal	Set retarder	Natural gypsum, chemical gypsum
Supplementary	Hydraulic blending materials	Materials with lime reactivity, such as natural pozzolanic rocks, burnt days, blast furnace slag, fly ash
Special Additives	Grinding acids, Hydrophobic agents, pigments	

5.3 CHEMICAL COMPOSITION OF RAW MIXES AND COMPOSITIONAL COMPATIBILITY

5.3.1 MODULE VALUES OF RAW MIXES

The composition of Portland cement clinker is represented by four major oxides. A combination of their ratios known as module values (Table 5.4) is used for the control of bulk chemical composition of clinkers. For convenience, these module values are extended to raw mixes as well. As a broad guideline the following rational limits have been proposed to the soviet cement industry for clinkers and corresponding raw mixes with coal ash influence.

Table 5.4: Module value used for clinker and raw mix

(S=SiO ₂ , A= Al ₂ O ₃ , F= Fe ₂ O ₃ , C=CaO, M= MgO, S= SO ₃)
Silica Modulus (M _S) = $\frac{S}{A+F}$
Alumina Modulus (M _A) = $\frac{A}{F}$
Hydraulic Modulus (M _H) = $\frac{C}{S+A+F}$
Lime saturation factor (LSF) = $\frac{100C}{2.8S+1.1A+0.7F}$ (when M _A <0.64)
Lime saturation factor (LSF) = $\frac{100C}{2.8S+1.65A+0.35F}$ (when M _A >0.64)
Lime saturation factor (LFSB) = $\frac{C-0.7s}{2.8S+1.2A+0.65F}$
Lime Standard (Ls) II = $\frac{100C}{2.8S+1.18A+0.65F}$
Lime Standard (Ls) II = $\frac{100(C+0.75M)}{2.8S+1.18A+0.65F}$ (when MgO<2%)
Lime Saturation III = $\frac{100(C+0.75M)}{2.8S+1.18A+0.65F}$ (when MgO>2%)
Lime – Saturation factor (LSF _R) = $\frac{C-(1.65A+0.35F+0.7s)}{2.8s}$ (when M _A >0.64)
$\Delta = 100 \frac{2.8s+1.65A+0.35F-C}{2.8S+A+F+C}$

5.3.2 EFFECT OF CHEMICAL COMPOSITION ON THE REACTIVITY AND BURNABILITY OF RAW MIXES

There are limitations; nevertheless, some of the effects of compositional variations are highlighted as follows.

1. Other conditions remaining the same, with increase in LSF, both reactivity and burnability of raw mixes are decreased at temperatures below the liquid formation, whereas above this temperature (1300°C) only burnability is decreased and reactivity is practically not affected. On the other hand, increase in silica modulus affects reactivity at all temperatures, while increase in alumina modulus get reflected primarily in harder burning.
2. In actual practice, one unit of LSF is regarded as equivalent of 20°C rise in burning temperature.
3. Alumina modulus is particularly critical in liquid phase sintering. In this context the points in Table 5.5 are of practical significance.

Table 5.5: Alumina modulus is particularly critical in liquid phase sintering

System	Liquid Formation Temperature °C	A/F Ratio for the Eutectic Composition	Fluxing Oxide
C-A-F-S	1338	1.38	Al ₂ O ₃ , when A/F < 1.38 Fe ₂ O ₃ , when A/F > 1.38
C-A-F-S-M	1301	1.63	Al ₂ O ₃ , when A/F < 1.63 Fe ₂ O ₃ , when A/F > 1.63

4. For the same silica modulus, the maximum formation of liquid at minimum temperature corresponds to the alumina modulus 1.38 or 1.63, depending on the MgO saturation, and for the same alumina modulus, the amount of liquid increases with decrease of silica modulus.
5. The general relationship of raw mix burnability with module value is illustrated in Fig. 5.3.

The reactivity of raw mixes is a resultant effect of

- dissociation of the mineral species into reacting oxides/complexes,
- transformation of the decomposed phases into a reactive state, and
- combination reactions.

5.4. PARTICLE SIZE OF GROUND MATERIALS IN RAW MIXES AND PHYSICAL PROPERTIES OF CLAYS

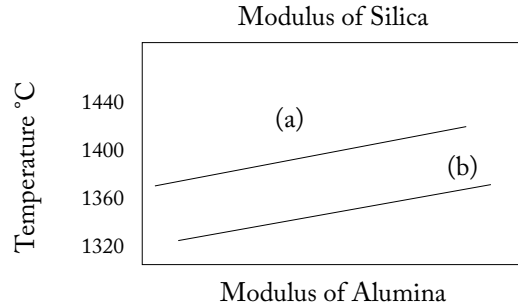


Figure 5.3: Effect of module values clinkering temperature and burnability.

5.4 PARTICLE SIZE OF GROUND MATERIALS IN RAW MIXES AND PHYSICAL PROPERTIES OF CLAYS

The particle size of raw mix is important for the very basic reason that the sintering rate is roughly proportional to the inverse of particle size. In general, the fineness of raw mixes varies in the range 3000–5000 cm²/g with about 9–22% particles or more than 0.07–0.09 mm and 0–5% over 0.2 mm size.

Properties like plasticity, specific surface, water requirement, suspension stability, coagulation of clay particles, swelling, etc. are of considerable importance in raw meal preparation, particularly in the wet process. Clays with at least 7–15 plasticity index and having 10% particles of +0.2 mm size and cumulative 20% particles of +0.08 mm size with CEC 11–12 mg/100 g are reportedly regarded as cement making variety.

5.5 SUMMARY AND CONCLUSIONS

1. The characterization and evaluation of raw materials for the manufacture of Portland cement have to be done necessarily in relation to the requirements of the manufacturing process and product quality, and their interrelation can be conceived as depicted in Fig. 5.4.
2. Although a wide variety of raw materials is used in cement industry, future trends would seem to use industrial wastes and to establish industrial complexes, based on a single set of raw material of another.
3. A limestone with a minimum 44–45% CaO and maximum 3–3.5% MgO, 0.6% K₂O, 0.6–0.8% SO₃, 0.25% P₂O₅, 0.5% Mn₂O₃, 1.3% TiO₂, and 0.015–0.02% Cl is regarded as a cement-grade limestone, provided its SiO₂, Al₂O₃, and Fe₂O₃ contents satisfy the ultimate module values of raw mixes. The compositional ranges of aluminofersilicate materials cannot be defined rigidly as they have to match the principal carbonate component. In general, a clay with more than 3% K₂O and 1% SO₃ may be considered, *prima facie*,

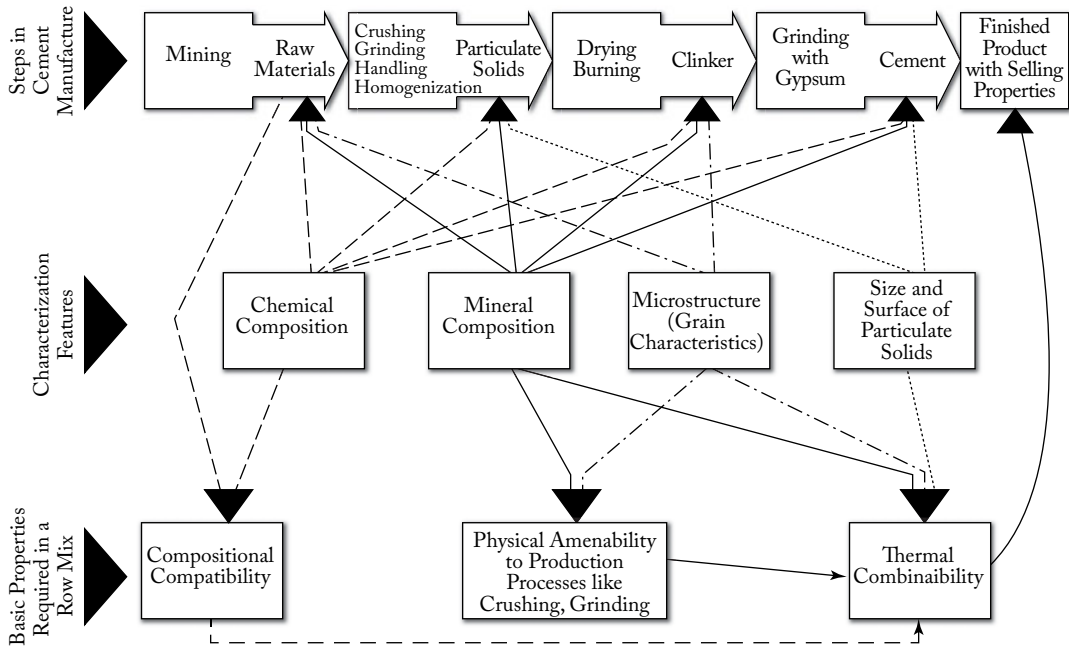


Figure 5.4: Interrelation of processing steps, characterization features, and basic properties of raw mixes in cement making.

unsuitable. For most of the minor constituents 0.5% is found to be a safe limit, in excess of which a special examination is called for.

- To arrive at a desirable raw-mix composition, clinker module ranges like 0.92–0.95 for LSF, 2.0–2.5 for M_s , and 1.4–1.6 for M_A may provide a rational guide.
- The thermal behavior of raw materials primarily depends on the activity state of the mineral species present in them. The temperature, rate, and activation energy of limestone dissociation depend on its mineralogy and microstructure. The rates of clinker formation reactions are also dependant on the mineral forms of the aluminofersilicate components of a kiln feed. The concurrence of carbonate dissociation and thermal demolition of aluminofersilicate component is considered a basic necessity for proper burning.
- The amenability of limestones to size reduction process is apparently controlled by the free and fixed silica content and the grain size variations of calcite and quartz, although a host of other factors also have a role to play.

7. The particle size distribution in ground raw mixes is critical both for burnability and clinker granulometry. The mineralogy of the coarser fractions of raw mixes is particularly significant for measure of their burnability. The limiting particle size for different mineral forms in raw mixes has already been evolved for easy burning.
8. Properties of the clay component are as important in cement making as those of the carbonate rocks. Since the clay composition is widely variable and its mineralogy is complex, the choice of clay is done more on the basis of its Si: (A, F) ratio, fusibility, and physical characteristics like plasticity granulometry, cation exchange capacity, etc.

Burnability and Clinkerization of Cement Raw Mixes

6.1 BURNABILITY

Burnability of raw mixes has been a matter of great importance in cement technology. The behavior of a raw mix during its sintering process is greatly influenced by its chemical, mineralogical and granulometric compositions, variation in these affect kiln operation, refractory lining, fuel consumption, and clinker quality. Each cement raw mix burns in its own way resulting in variation of clinker quality.

The burnability of a cement raw mix conceptually denotes the amount of mass transfer of its constituents with ease or difficulty to the clinker phases. By convention, burnability is measured by determining the CaO_f (free) after burning the raw mix for a certain time (θ) at a certain temperature (T), i.e., $\text{CaO}_f = F(\theta, T)$, above 1300°C when melt is formed, burn ability decreases by increasing this parameter.

Burnability is generally expressed by either of the following two quantities.

1. Measure of CaO_f of a pseudo-isochrones ($\theta = \text{constant}$) at a given temperature. Increasing values of CaO_f correspond to decreasing burnability.
2. Measure of time (θ) of pseudo-isotherm ($T = \text{constant}$) for $\text{CaO}_f \leq 2\%$, increasing of θ corresponds to decreasing burnability.

The following are the important parameters which affect the burnability of a raw mix to a great extent.

1. Raw mix-mineralogical composition:
 - Lime components: consisting mainly of CaCO_3 and very small quantity of the following in order S-M-R:F:S:N:K.
 - Clay components: consisting mainly of SiO_2 with considerable amount of the following in the order R:F:C-M-S-N-K.
 - Corrective ingredients: consisting mainly of other of any main oxides (C/A/S/F).
 - Modifiers: consisting of different inorganic compounds which accelerate the clinkization reactions.

2. Raw mix-chemical composition:

- Main component oxides are: C, A, S, and F.
- Minor volatiles are: K, N, S, P, F, Cl, and H.
- Minor non-volatiles are: S_f , M, Ti, Mn, Sr, and Cr. Each component of the raw mix has individual and combined (M_s , M_A , LSF, and M_s) effect on burnability.

3. Raw mix-granulometric composition: fineness and particle size, distributions, homogeneity, and compaction.

- The more fine grained, the greater surface area a raw mix has, the easier it is to sinter and the lower the sintering temperature.

Homogenization of kiln feed is a major operation in cement manufacturing as it affects the quality of clinker, burning process, and fuel consumption. Fluctuation of the kiln feed measured as % CaCO_3 should not be more than ± 0.2 from the holding point. An increase of 1% CaCO_3 will increase the C_3S by 13% and reduce C_2S by about 11.5%. The ultimate homogeneity depends on the physical-chemical characters, fineness and particle size distributions, method of mixing, and efficiency of the blending system.

4. Raw mix-thermal treatment:

Firing temperature: in clinker the temperature must be fairly enough for the formation of alite phase. Burning of the raw mix is generally carried out at 1450–1500°C. Excessively high burning temperature results in a great stress on the kiln and the refractory lining, more fuel consumption, reduction in cement strength, and larger alite crystals. Increase in burning temperature from 1360–1420°C results in lowering the burning period by half. Maximum firing temperature was determined by a multiple regression analysis of raw meal containing only the four main oxides as given below:

$$^{\circ}\text{C} = 1300 + 4.51 \text{C}_3\text{S} - 3.74\text{C}_3\text{A} - 12.64\text{C}_4\text{AF}.$$

- (a) Holding time: on increasing holding time, the following changes may be observed.
- i. C_3A content decreases and C_4AF content increases.
 - ii. C_2S decreases and C_3S increases.
 - iii. Higher mechanical strength at later ages and lower at early ages.
 - iv. Heat of hydration at early ages decreases.
 - v. Unburnt clinker can produce high-quality cement even in presence of high CaO_f .
- (b) Burning rate: rapid burning is always favored for the following reasons.
- i. More coarse-grained materials can be charged.

- ii. Materials differing by their degree of fineness can be charged.
 - iii. Five grains of C_2S formed which accelerate the interaction of C_2S , CaO_f and liquid.
- (c) Burning activation: thermal activation may be enhanced by either accompaniment with mechanical (vibratory mill) or chemical (mineralizer) activation. Mechanical activation gives better results than chemical.
5. Liquid phase formation: appearance temperature, amount, viscosity, surface tension, ionic mobility:

A, F, M, minor volatile and non-volatile components generally govern the amount of liquid formed, its appearance, temperature, viscosity, surface tension, and ionic mobility in the clinkerization process. The range of clinker composition may be fairly wide if the amount of liquid phase increases slowly. A clinker with about 25% liquid phase form a raw mix is generally considered an ideal raw mix for kiln lining, fuel saving, rapid C_3S formation through dissolution of phase at $1450^\circ C$ is usually calculated by

$$3.0A - 2.28F + K + N + M \quad \text{when } M_A > 1.38$$

$$8.5A - 5.22F + K + N + M \quad \text{when } M_A < 1.38$$

6. Clinker quality: silicate phase, alumina-ferrite phases.

It has been seen that the burnability becomes worse as the potential C_3S content increases, at the expense of other clinker constituents, while increasing C_3A and C_4AF content, the burnability improves, and the C_4AF is significantly more effective in this respect.

7. Coal ash: amount absorbed, composition, fineness.

When coal is used as the fuel for clinker-making, its ash quantity, composition, and fineness affect the burnability. Generally, the composition of coal ash varies within the limits: S-35-60%, A-15-35%, F-5-20%, C-0-10%, and M, S and alkalis are often present in the ash in small amounts. In general, the ash composition shows a very high S/C ratio and moderately high A/F ratio.

8. Kiln atmosphere: oxidation, reduction.

Reducing conditions during cement clinker burning substantially affect the color of the clinker by producing Ferrous oxide, accelerate the setting by enhancing C_3A content at expense of C_4AF , and reduce the strength by breaking down C_3S during clinker cooling. Therefore, oxidizing conditions (0-1-2 vol. % in exist gas) should be maintained in the kiln for better clinker quality.

6.2 REACTIVITY

Reactivity of a raw mix is defined by the overall chemical reactions among the represented constituents of the raw mix, attained on burning it at a certain temperature for a certain time, i.e., $R_m = F(T, \theta)$, above 1300°C when melt is formed, this parameter, however, has no effect on reactivity.

Factors Affecting Reactivity

1. Physical-chemical, mineralogical, and granulometric composition.
2. Chemical process of clinker mineral formation.

6.3 REACTION SEQUENCE

The course of reaction inside a rotary kiln has been of great interest to the cement technologists since the kiln is controlled by computer and, obviously, a mathematical model to explain the reaction process is to be constructed in order to find a logical relation between the process variables.

Table 6.1: Zone temperature range 0°C and reaction profile

I	Up to 200	Evaporation (slurry drying) preheating
II	200–800	(dehydration, dehydroxylation, and first appearance new phases).
III	800–1100	
IV	1100–1300	Decarbonization (calcinations) exothermic
V	1300–1450–1300	reactions sintering cooling
VI	1300–1000	

The experimental observations revealed the following phenomena.

1. The first aluminate phase “CA” is formed at lower temperatures (550–600°C) which, in turn, combine with free CaO resulting in the formation of an intermediate phase $C_{12}A_7$ and finally it converts into C_3A above 900°C.
2. The formation of C_2AS as an intermediate phase is likely but dependent on the nature of raw materials used.
3. The ultimate formation of C_4AF at higher temperature (1300–1440°C) is consecutively followed by the appearance of ferrite phase (CF and C_2F) at lower temperature (800–900°C).

Parallel observations, which confirmed the above items.

1. The reaction sequence of raw mixes is almost identical in dry, semi-dry, and wet kiln.
2. The dissociation and decarbonation of raw-mix components start at 550–600°C. The CaO formed during decarbonation reacts with other components simultaneously in such a way that about 2% CaO_f at 800°C and about 17% at complete decarbonation temperature (1000°C) remain unreacted.
3. The first detectable phases CA+C₁₂A₇+C₂S were noticed at 7000°C. The amount of these phase increase with temperature up to 900–1000°C, when poorly detectable C₃S and some C₄AF/C₂F are traced.
4. In some other investigations, the first phases detected are CF+CA+CS which are subsequently converted into clinker phases with rise of temperature in accordance with the following scheme:

$$\begin{array}{l} \text{CA} \text{_____} \text{C}_{12}\text{A}_7 \text{_____} \text{C}_3\text{A} \\ \text{CF} \text{_____} \text{C}_2\text{F} \text{_____} \text{C}_4\text{AF} \\ \text{CS} \text{_____} \text{C}_3\text{S} \text{_____} \text{C}_2\text{S} \end{array}$$
5. X-Fe, FeO, and Fe₂O₃ along with the temperature of x-wolestonite almost concurrently with B-C₂S are detected from a series of charge samples.
6. Extensive study made after comparing five kiln charges coating a reaction sequence was derived accordingly, as shown in Fig. 6.1, which further confirmed the above observations.

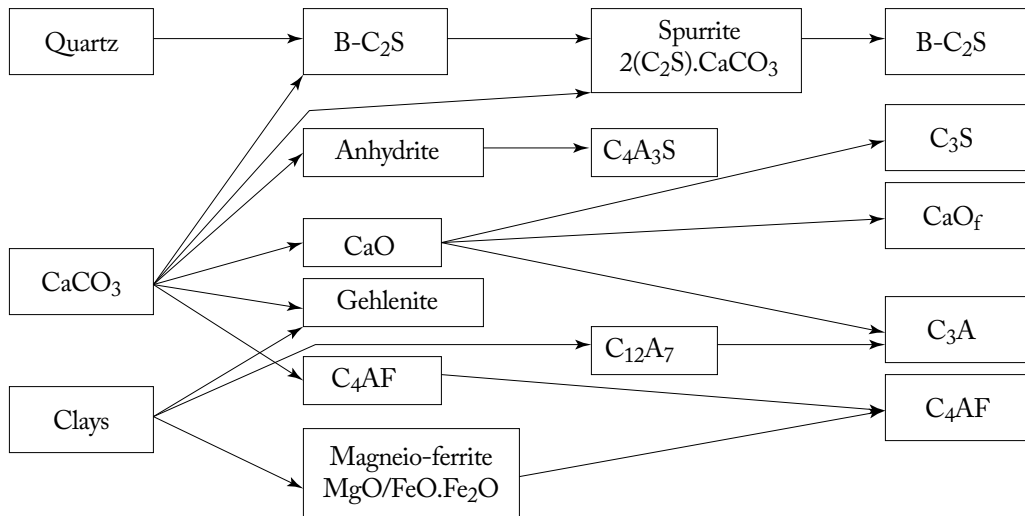


Figure 6.1: Reaction sequence in cement rotary kiln.

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7. The solid reactions are almost complete at a temperature of about 1300°C and a melt phase appears. The melt phase contains a complete melting of $C_3A + C_4AF$ and partial melting of C_2S and CaO with incorporation of such constituents as R_2O , MgO . The formation of C_3S is activated through clinker phases appear with the formation C_3A , C_4AF , C_2S , C_3S , MgO , and glass after crystallization of the residual liquid.

Manufacturing Portland Cement

The manufacture of cement [2] is composed of two independent processes.

Fabrication of the intermediate product—the clinker, which includes preparation of the raw mixture and firing of it and the grinding of the clinker together with the admixtures, storing and packing of the Portland cement.

There exist two methods for preparing raw mixture: a wet method and a dry method. Both are outlined in this chapter.

7.1 DRY PROCESS

The specific feature of this process is that the raw materials are ground and mixed in the dry state. In this process, limestone and clay are ground separately to fine powders and then mixed together in the desired proportions. Water is then added to it so as to get a thick paste of which cakes are then made, dried, and burnt in kilns. To the clinker obtained after burning is added 3–4% of gypsum and ground to very fine powder. This powder is cementing ready for use. This process is slow, costly, and also difficult to have the correct proportion of constituents; to do so is a cumbersome operation. The quality of cement is not as good as that of the one manufactured by wet process. This method has therefore become obsolete.

7.2 WET PROCESS

The specific feature of this process is that the raw materials are prepared in water. The flow diagram of the wet process for manufacturing Portland cement is given in Fig. 7.1.

Mixing: The limestone is first broken up in crushers (2), and a liquid mass from clay mixer (1), which are in desired proportions are fed into ball mill (raw-material mill (3)), and are simultaneously ground to very fine powder and water is added to it. Ball mill (shown in Fig. 7.2) is a rotating steel cylinder in which there are hardened steel balls. When the mill rotates the steel balls pulverize the raw materials which form into a solution with water. This liquid mixture is known as a slurry. This slurry is then passed into storage tanks known as silos (correcting slurry basin (4)), where it is stirred with agitators or by pneumatic mixing. The slurry is passed to horizontal basin (5), where the proportioning is finally adjusted to ensure the correct chemical

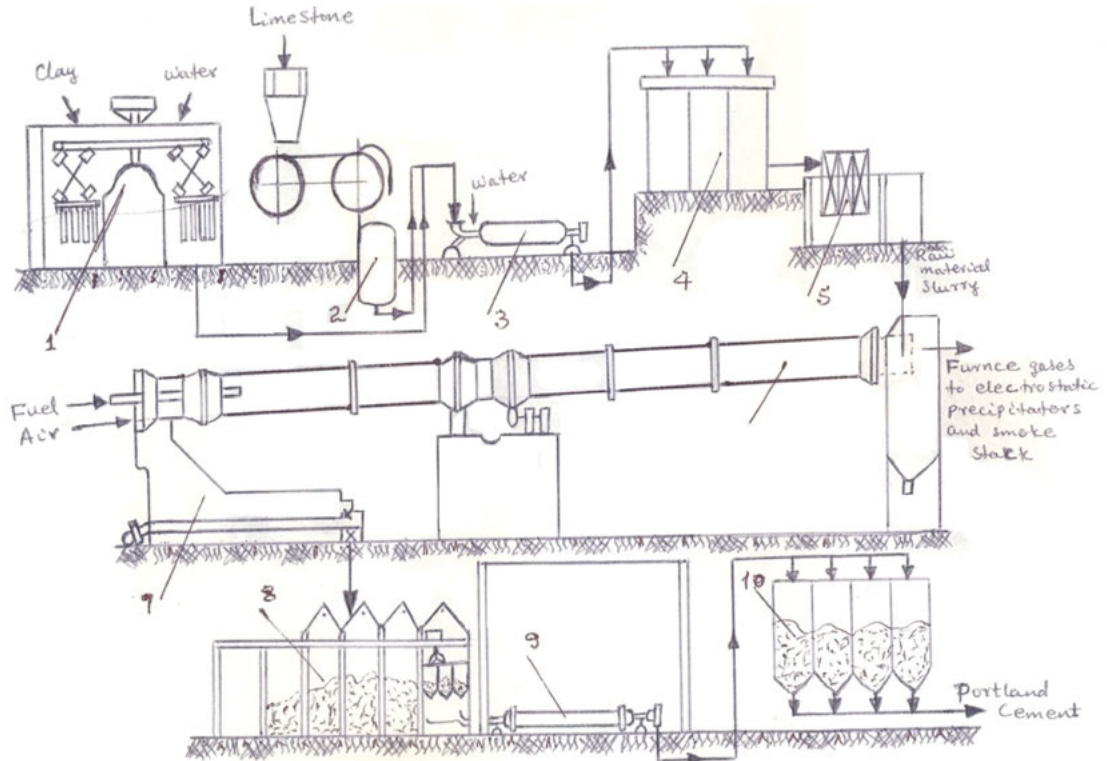


Figure 7.1: Flow diagram of Portland cement manufacturing by wet process: (1) clay mixer, (2) hammer crusher, (3) raw material mill, (4) correcting slurry basin, (5) horizontal slurry basin, (6) rotary drum furnace, (7) grate cooler, (8) storage, (9) cement mill, and (10) cement silos. (Hand-drawn by the author.)

composition, and to obtain the necessary ratio of compounds (components). Composition of raw mix in the wet process can be better controlled than in dry process. The corrected slurry is then fed into the rotary kiln for burning.

Burning: The corrected slurry is fed at the higher end of the inclined rotary kiln (rotary drum furnace (6)) shown in Fig. 7.2, whereas from the lower end of the kiln a flame is produced (using combustion products) by injecting pulverized coal with a blast of air, and that moves through it in a counter current of hot gaseous. The rotary kiln is a steel tube lined inside with fire bricks.

It goes to 120 m long and from 2.5–3.5 m in diameter. The kiln is mounted on rollers at a gradient of 1 in 25 to 1 in 30 and rotating once in every minute. The slurry interaction results in the successive processes of water evaporation, mineral dehydration, dissociation of limestone, and chemical reactions between the basic oxides, CaO, which is formed, and the

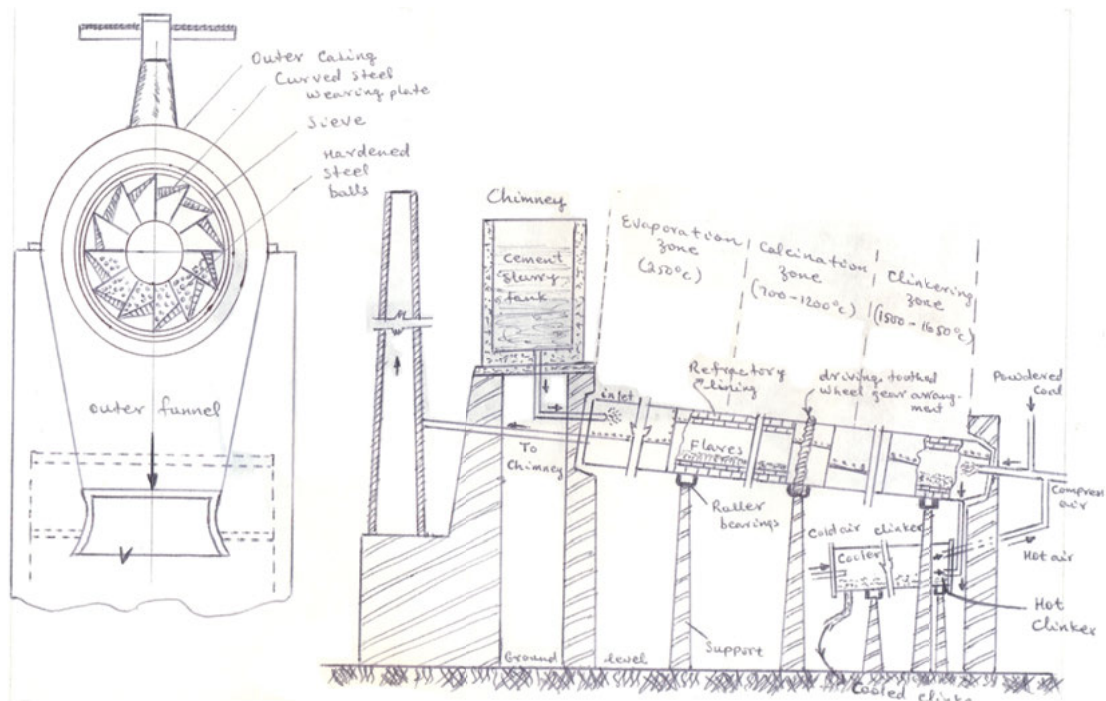


Figure 7.2: Cross section of a ball mill and rotary kiln. (Hand-drawn by the author.)

components of the clay SiO_2 , Al_2O_3 , Fe_2O_3 , and finally small lumps or “nodules” are fired. The nodules gradually roll down passing through zones of rising temperature until they reach a burning (sintering) zone where they are finally burnt at $1500\text{--}1650^\circ\text{C}$. At this temperature “nodules” change to clinkers. The clinker is cooled with cold air in grate type cooler (7), to temperature of $50\text{--}60^\circ\text{C}$. In these coolers, which are located below the kiln, the air is passed up through a bed of clinker particles uniformly distributed on a bar grating.

Grinding: The clinker is transferred from the coolers to the storehouse (8), where it is kept for a certain length of time for quenching (hydration) of free lime. The cured clinker together with hydraulic or inert admixtures and gypsum, which is added to control the setting time, is ground in tubular cement mills (9). The cement is stored in reinforced concrete silos (10), through the bottom of which air is forced when the cement is being discharged to loosen it. Cement is delivered to consumers in automobile or railway cement tanks in bulk or in paper multilayer bags.

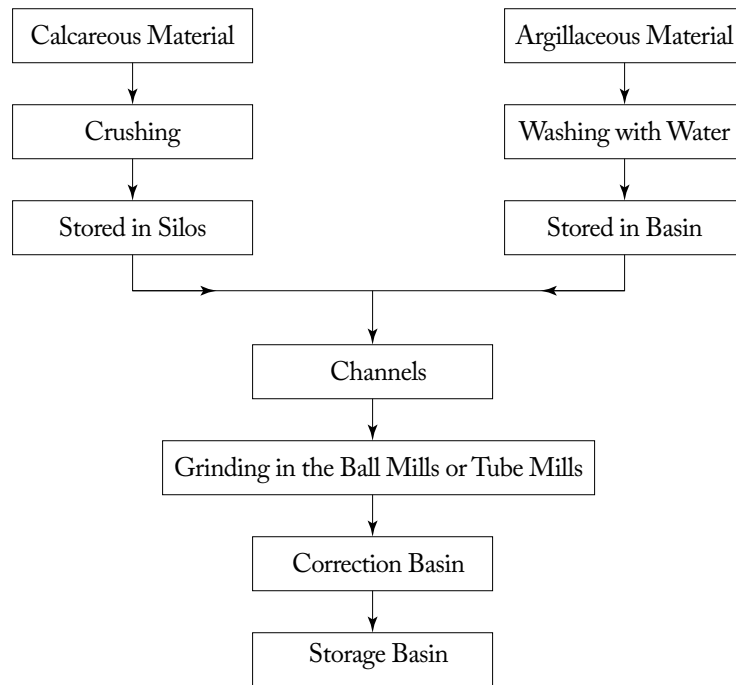


Figure 7.3: Flow diagram of cement manufacture (wet process).

Testing Portland Cement

8.1 SAMPLES FOR TESTING

Each sample for testing shall consist of an intimate mixture of approximately equal portions selected from at least 12 different bags or packages when the cement is not loose or 12 different position in the heap or heaps when the cement is loose. Selection of samples shall be done in such a manner so as to obtain a fair average sample. The sample taken will be stored in an airtight container until the time of the test.

8.2 CHEMICAL COMPOSITION

Loss of ignition: Heat 1.00 g of the sample for 15 m in a platinum crucible (or for 1 h in porcelain crucible) at a temperature of 900–1000°C. Cool and weightloss on ignition should not be more than 4%.

Insoluble residue: Boil for 10 m a well-stirred mixture of 1 g cement, 40 cc of water and 10 cc concentrated hydrochloric acid (sp.gr.1.18). Filter the solution and rinse the container five times and wash the filter ten times with hot water. Wash the residue on a filter with hot water and boil for 10 min with Na₂CO₃ solution (2N). Filter the solution again through the same filter paper and wash five times with water. It is now washed with HCl (2N) and finally with water until it is free from chlorides. The filter paper should be dried ignited and weighed to give the insoluble residue. The insoluble residue should not be more than 1.5%.

Lime and alumina: The percentage of lime to silica, alumina, and iron oxide when calculated by the formula

$$\frac{\text{CaO} - 0.7\text{SO}_3}{2.8\text{SiO}_2 + 1.2\text{Al}_2\text{O}_3 + 0.65\text{Fe}_2\text{O}_3}$$

should not be greater than 1.02 nor less than 0.66. The ratio of the parentage of alumina to that of iron oxide shall not be less than 0.66. An excess of free lime will cause unsoundness of cement.

Magnesia: If free magnesia exceeds 5% then it makes the cement unsound.

8.3 FINENESS

Finer cements react quicker with water and develop early strength, although the ultimate strength is not affected. However, finer cements increase the shrinkage and cracking of concrete. The fineness is tested by either one of the following two methods.

1. By sieve analysis: break with hands any lumps present in 100 g of cement placed in a sieve No. 9, and sieve it by gentle motion of the wrist for 15 m continuously. The residue when weighed should not exceed 10% by weight of the cement sample.
2. By specific surface: will not be less than 2250 cm²/g as found by Wagner's turbidimeter method.

8.4 CONSISTENCY OF STANDARD CEMENT PASTE

The following physical test should be carried out, whenever possible, between the temperate range of 25–29°C.

This test is performed to find out the correct amount of water to be added to a given quantity of cement so as to get a paste of normal consistency. This test precedes the test of cement for soundness, setting time, and tensile strength or for compressive strength. This test can do with the help of vicat's apparatus having the frame movable rod, as shown in Fig. 8.1. Diameter of the rod mostly is 1 cm and is 5 cm long. At its lower end is attached a detachable needle 1 mm square or 1.3 mm in diameter and 5 cm long. There is a vertical scale graduated from 0–40 mm in either direction to measure the vertical movement of the rod.

To start with 25% of clean water is mixed with about 300 g of neat cement in a crucible. The mixing can be done with a standard spatula shown. After about 30 s it is thoroughly mixed with hands for at least 1 min. The kneaded paste is tossed about six times from one hand to the other and pressed into the hard rubber mold through its bigger end. Fill the mold completely with paste and remove the extra paste by a single movement of the palm. Place the inverted mold (with larger end on glass plate) and slice off extra paste from top by a single movement of trowel. Place to mold resting on glass plate under the needle. Bring 1 cm diameter end of needle in touch with the paste and release it without any jerk or force and note the penetration. The time taken from adding of water in cement to filling of mold should be between 3–5 min. Repeat experiment with trial pastes made with varying percentages of water. The paste giving a penetration of 33–35 mm is said to be of normal consistency. The amount of water mixed is expressed as a percentage by the weight of dry cement. This is usually in the neighborhood of 30% for a paste of normal consistency.

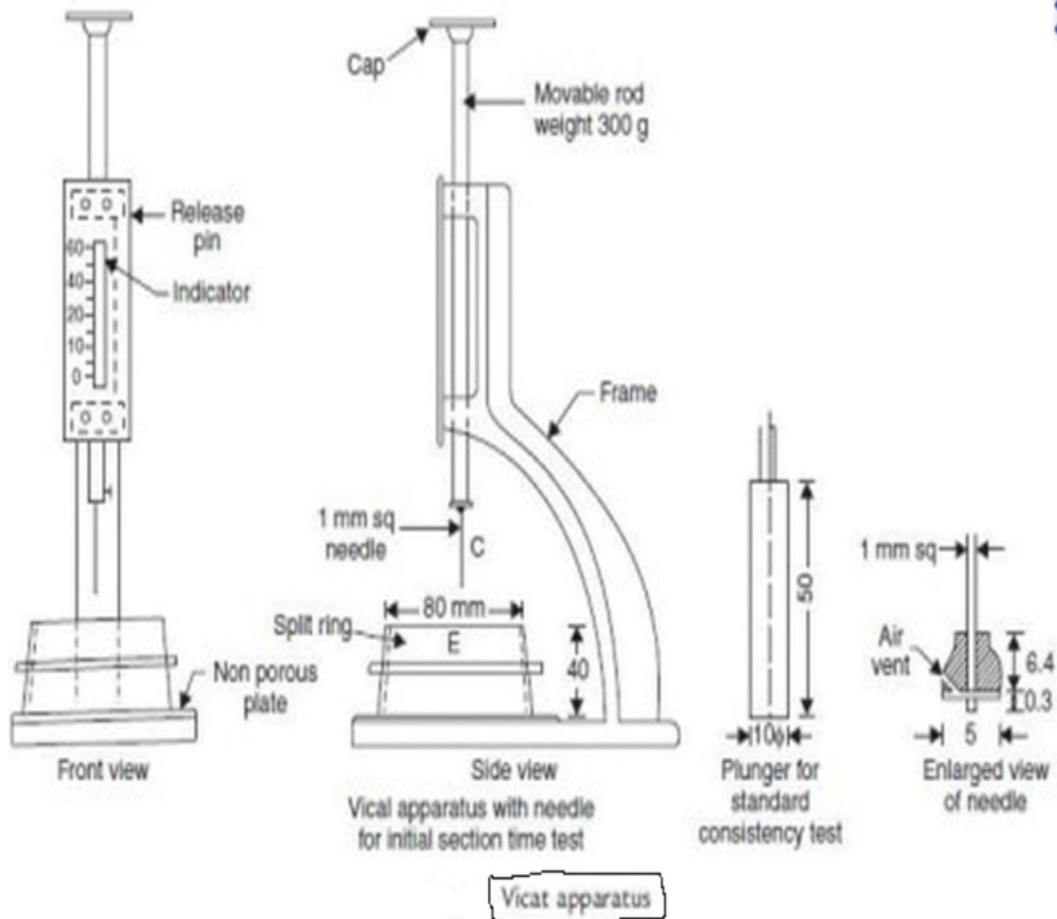


Figure 8.1: Vicat apparatus.

8.5 SOUNDNESS

It is essential that cement concrete does not undergo large changes in volume after setting. This change in volume is known as unsoundness and may cause cracks, distortion, and disintegration of concrete.

The test is carried out with the help of Le Chevalier's apparatus shown in Fig. 8.2. It consists of a split brass cylinder 30 mm high, 30 mm internal diameter, and 0.5 mm thick. Two pointers AA, 165 cm in length up to the axis of cylinder, are attached to the cylinder, one on each side of the split. Cement paste prepared with 0.78 times the water required preparing a paste of normal consistency and 100 g of cement is filled in the mold resting on a glass plate. Another glass plate is placed on the mold and weighed down. The whole is immediately placed

is filled in the mold at the lower end of the rod is fitted with a 1 mm square needle. This needle is brought in contact with the surface of paste and released. The initial set is said to have taken place when the needle fails to penetrate beyond a point 5 mm above the glass plate. The time taken from the instant can added to cement to the moment when the needle fails to penetrate 5 mm before the glass plate is known as it should not be less than 30 m for ordinary Portland cement.

For finding out the final setting time the 1 mm square needle is replaced by the other needle. This needle has an annular attachment around 1 mm square needle and projecting by 0.5 mm below it. To find final setting time the needle shall be brought in touch with the paste in the mold and released instantly. The final set shall be considered as having taken place when the attachment fails to make any impression on the surface of paste whereas the needle makes one. The time from the moment water was added to make impression on the surface of cement paste is known as final setting time.

For ordinary Portland cement the final setting time should not be more than 10 h. The test should be performed in an air-conditioned room with 90% humidity and at a temperature between 25–29°C.

8.7 COMPRESSIVE STRENGTH

The compressive strength of cement is judged by finding the compressive strength of cement and sand mortar. For the purpose on part by the weight of cement is mixed dry with three parts by weight of IS sand. To this dry mixture of cement and sand is added water given by the following formula:

$$P = \frac{Pn}{4} + 3.5,$$

where P is the % of water by weight of dry materials and Pn is the % of water required for making a cement paste of normal consistency.

Cement sand and water shall be intimately mixed to give the paste of uniform color but the mixing should be intimately mixed to give the paste a uniform color but the mixing should not be for more than 3–4 min. Cubes of 7.06 cm sides are then molded out of this paste and are kept in an atmosphere to 90% humidity and 25–29°C temperature for 24 h. They are then removed from the molds and kept submerged in clean water until the time of the test and should not be allowed to dry.

Three webs each are tested in a compression testing machine after 3 days and 7 days. Compressive strength of ordinary Portland cement should not be less than the following values:

After 3 days	115 kg/cm ²
After 7 days	175 kg/cm ²

8.8 TENSILE STRENGTH

Tensile strength of cement sand mortar is tested to judge the tensile strength of cement. To do so briquettes of standard dimensions are prepared. Briquettes have a uniform thickness of 25.1 mm and a minimum sectional area of 645 mm² at the central section. For preparing briquettes one part by weight of cement and three parts by weight of water are mixed with the quantity of water found from the following formula,

$$P = 0.2Pn + 2.5.$$

Cement sand and water are mixed intimately so as to get a uniform of the mortar. A small heap of mortar is placed on a briquette mold and filled as usual. It is then beaten down with the standard spatula until water appears on the surface. The mold is now turned upside down and as before again a small heap of mortar is placed and beaten down. The surfaces are smoothed with the blade of a trowel. The briquettes are taken out of moulds after keeping them in an atmosphere of 90% humidity and temperature of 25–29°C for 24 h. Six such specimens each are tested in a briquette testing machine after 3 days and 7 days.

Tensile strength for good Portland cement should be as follows:

After 3 days	not less than 20 kg/sq cm
After 7 days	not less than 25 kg/sq cm

Hydration of Portland Cement

The hydration behavior of Portland cement [4] encompasses that of its constituent minerals, but care must be taken in translating their functioning to that of practical Portland cement systems. While a number of studies have tended to approximate, the hydrations of alite with that of Portland cement, many additional criteria are involved. Not least of these are interactive relationships between the principal hydrating minerals C_3S , C_2S , C_3A , and C_4AF . None of these phases is pure; each contains a large number of elements in small quantities in solid solution. Alkalis can and do affect the course of the reaction, whether percent as water-soluble sulphate or incorporated in the constituent phases initially with exsolution occurring during hydration. The products formed (C-S-H, ettringite (the reaction product of C_3A with gypsum), mono sulphate- C_4AH_{13} , Calcium hydroxide, etc.) are also impure. Analytical electron microscopy of cement pastes has shown that C-S-H incorporates significant amounts of aluminum, iron, and sulphur, while the ettringite and MonoSulphate phases contain significant amounts of silicon, and even the calcium hydroxide contains small quantities of foreign ions chiefly silicate. There is no pure saturated solution of calcium hydroxide, for instance a whole host of other cations and anions in different quantities (mostly small) are also present. The permutation and combination of what can and does occur in practice are, of course, infinite and it must not be forgotten that hydrating Portland cements are exceedingly complex systems with many interactive possibilities. In the processes for shortening the hardening time can be classified as follows.

1. The use of quicker hardening cements such as high early strength cement.
2. Heat treatment methods.
3. The use of electromagnetically treated mixing water.
4. The use of chemical additive as hardening accelerators.
5. The use of pressure.

For optimum effects the magnetizing parameter, such as the magnetic field strength, the flow rate of the water and the period of influence of the field on the water must be accurately determined.

Different Kinds of Cement

The following are some of the important kinds of cements manufactured to suit the different requirements.

10.1 RAPID HARDENING OR HIGH EARLY STRENGTH CEMENT

This cement gains strength faster than the ordinary Portland cement. Its initial and final setting times are the same as those of ordinary cement. It contains more of tri-calcium silicate and is more finely ground. It gives out more heat while setting and is as such unsuitable for mass concreting. It is used for such structures as are to be subjected to loads early, e.g., repair of bridges and roads, etc.; it is more costly than the ordinary cement. It is manufactured by burning at clinkering temperature an intimate mixture of calcareous and argillaceous materials and grinding the resultant clinker without the addition of gypsum and not more than 1% air entraining agents.

The average compressive strength of at least three mortar cubes (area of face 50 cm²) composed of one part cement and three parts standard sand by mass p*/4+3 percent (of combined mass of cement and sand) water, shall be as under:

After 24 h	not less than 160 kg/cm ²
After 72 h	not less than 275 kg/cm ²

P* is the % of water required to prepare a paste of standard consistency.

10.2 HIGH ALUMINA CEMENT

It is manufactured by fusing together a mixture of bauxite and limestone in correct proportion and at high temperatures. The resulting product is ground finely. It develops strength rapidly and is of black color and resists well the attack of chemicals especially of sulphates seawater. Its ultimate strength is much higher than that of ordinary cement. Its initial setting time is more than 2 h and the final set takes place immediately thereafter. Most of the heat is given out by it in the first 10 h as a result of which it can be conveniently used in freezing temperatures but it used in thin layers in normal temperatures.

10.3 QUICK SETTING CEMENT

It sets faster than the ordinary Portland cement. Its initial setting time is 5 m and the final setting time is 30 m. It is used for making concrete that required setting early, as for laying under water or in running water. Initial setting time being very little there is always the danger of concrete having undergone initial setting during mixing and placing as such this cement is used only in exceptional circumstances.

10.4 PORTLAND SLAG CEMENT

It is obtained by mixing Portland cement clinker, gypsum, and granulated slag in proper proportion and grinding it finely. This cement has properties very much similar to those of ordinary Portland cement with the following improvements.

1. It has less heat of hydration.
2. It has better resistance to soils, sulphates of alkali metals, alumina, and iron.
3. It has better resistance to acidic waters.

This cement can advantageously be used in marine work. Manufacture of Portland slag cement is aimed primarily at profitably utilizing blast furnace slag—a waste product from blast furnaces

10.5 LOW HEAT CEMENT

Heat generated by cement while setting may cause the structure to crack in case of concrete. Heat generation is controlled by keeping the percentage of tri-calcium aluminates and tri-calcium silicate low. Its initial and final setting times are nearly the same as those of ordinary cement but the rate of its developing strength is very slow. It is not very suitable for use in ordinary structures, when not only the use of structures shall be delayed but also the shuttering shall have to be kept for long and curing will be prolonged.

10.6 AIR ENTRAINING PORTLAND CEMENT

It is ordinary Portland cement mixed with small quantities of air entraining materials used are: resin, vinsol resin, oils, fats, and fatty acids. Vinsol resin and darex are most commonly used. These materials have the property of entraining air in the form of fine air bubbles in concrete. These bubbles render the concrete more plastic, more workable and more resistant to freezing. However, because of air entraining the strength of concrete reduces and as such the quantity of air so entrained should not exceed 5%.

10.7 WHITE CEMENT

It is cement with pure white color and having the same properties as those of ordinary Portland cement. Grayish color of ordinary cement is due to iron oxide, as such white cement is manufactured from white chalk and clay free from iron oxide. Oil fuel and not the coal are used for the burning of this cement. It much more costly than ordinary cement.

10.8 COLORED CEMENT

By mixing suitable pigments ordinary Portland cement could be given a red or brown color. For other colors, 5–10% of desired pigments are ground with white cement. Pigments used in cement should be chemically inert and durable so as to fade due to the effect of light or weather.

10.9 PORTLAND POZZOLANA CEMENT

Portland pozzolana cement is produced either by grinding together Portland cement clinker and pozzolana (porous volcanic rock) or by intimately and uniformly blending Portland cement and fine pozzolana.

This cement has properties similar to those of ordinary Portland cement, and can therefore be used for all general purposes where the latter is employed, with no change in the proportion of coarse or fine aggregates and cement. Gypsum can be added in both cases.

Portland pozzolana cement produces less heat of hydration and offers greater resistance to the attack of aggressive waters or cusplate-bearing soils than ordinary Portland cement. It also reduces leaching of calcium hydroxide liberated during the setting and hydration of cement. Consequently, Portland pozzolana cements concrete structures.

Pozzolana cement takes a little longer than ordinary Portland cement to gain strength. It is recommended that when pozzolana cement is used in reinforced concrete, the centering be left in position a little longer than would be the case with ordinary Portland cement. Ultimate strength of this cement is more than that of ordinary Portland cement but initial and final setting times are the same.

10.10 CHEMICALLY INERT (ACID-RESISTANT) CEMENTS

It can be divided into acid-resistant cements, concretes, and putties. Acid-resistant cement is made without firing from silicate or soluble glass (an aqueous solution ion of the silicates of alkali metals with a common formula $Ck, Na_2O.nSiO_2$), finely ground acid-resistant aggregates (andesine, diabase, quartz), and sodium fluosilicate Na_2SiF_6 . Depending on the aggregate used acid-resistant cements are called quartz cement, landsite cement, etc.

Cement powder consists of a mixture of pulverized aggregate and sodium fluosilicate. When this mixture is combined with liquid glass, the mass formed soon sets and then rapidly hardens. Setting and hardening take place as a result of the reaction between the liquid glass and

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sodium fluosilicate leading to formation of silicon acid gel (H_4SiO_4) which possess bonding properties.

Acid-resistant cements are used for lining chemical equipment and for preparing mortar and concretes. When a piece of equipment (acid-storage.vat acid absorption tower, reactor, etc.) is lined, polyisobutylene or rubber is glued on to the shell walls and the acid-resistant lining is applied on top of this film to provide complete tightness of the lining. Acid-resistant putties, used in assembling chemical apparatus, are also made from acid-resistant cements.

Storage of Cement

Portland cement is a finely ground material. It therefore readily absorbs moisture even from the atmosphere. It is therefore essential to protect it from dampness during storage. Lack of proper care may cause setting of cement or reduction in its strength due to partial setting. Following precautions must as such be taken in storing cement.

1. Walls, roof, and floor of the building in which cement is to be stored should be completely waterproof.
2. In case the cement store is newly constructed then its interior should have been thoroughly dried before cement is stored on it.
3. Doors and windows should be properly titted and should be kept shut.
4. Except in the case of dry concrete floor the cement bags should be stacked on wooden planks.
5. The bags should be stacked away from walls. A space of 25 cm all around should be left between the exterior walls and the piles.
6. Bags should be piled close together.
7. Bags should be piled in header stretcher fashion and not more than 15 bags high.
8. While removing cement from store do not take out bags from one tier only. Step back two or three tiers.
9. Each incoming consignment should be stacked separately and a placard bearing the date of arrival of the consignment should be pinned to it. This would help in using cement in the same order as it arrives thereby avoiding dead storage, that is a stack remaining in position for a long time while other consignments of cement come in and go out.
10. For temporary storage of cement at the site of work, bags should not be stacked on the ground. A minimum number of bags needed should be piled upon a raised, dry platform and covered with tarpaulins.

Technical Analysis of Cement

Cement has to be produced in quantity to meet the need it has to have standard quality [1]. Cement analysis is mainly done to control its quality. Various constituents affect the quality of cement (cement has an ideal composition). The following formula can be used to calculate the percentage or kg wt. of constituent provided the rest are as follows.

Given:

$$K = \frac{a(b - c)}{(b - d)},$$

where

K = kg of calcined limestone

a = kg of clinker to be made

c = percent of CaO in clinker

d = percent of CaO in calcined limestone

b = percent of CaO in ignited shale

Example: Suppose that a calcined limestone contains 96% CaO, ignites shale contains 4% CaO, and the desired clinker is 65% CaO. If 100 kg of clinker is to be made, what amount of calcined limestone and ignited shale are required?

Solution:

$$K = \frac{a(b - c)}{(b - d)}$$

Given:

$a = 100$ kg

$b = 4\% = 0.04$

$c = 65\% = 0.65$

$d = 96\% = 0.96$

Then,

$$K = \frac{100(0.04 - 0.65)}{(0.04 - 0.96)} = 66.3 \quad \text{kg of calcined.}$$

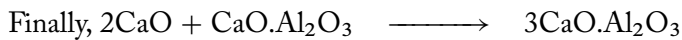
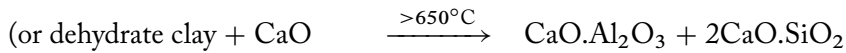
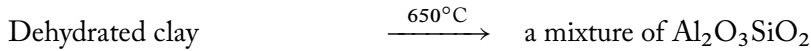
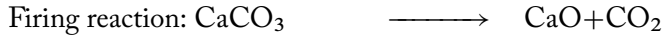
Limestone: Since the clinker is calcined limestone plus ignited shale, the amount of ignited shale required is: $100 - 66.3 = 33.7$ kg.

Within certain definite limitation in composition of cement, the mixture behaves satisfactorily in kilns and produces good cement; outside of these limits it is also shown that trouble in burning may result or the cement may be of inferior quality.

There are possible defects arising from unbalanced composition. For instance; if the lime content is too high, the extra lime does not come in to combination, and this may cause expansion and cracking of the mortar or concrete. Silica, alumina, and ferric oxide are likewise limited. If the lime content is fixed, and silica becomes too high, which may be accompanied by a decrease in alumina and ferric oxide, the temperature of burning will be raised and the special influence of the high lime is lost. If the lime is too low which means an increase in the alumina ferric oxide, the cement may become quick-setting and contain larger amount of alumina compounds which appear to be of little value for their cementing qualities. The magnesia (MgO) content is limited, not to exceed 5% because higher magnesia may be dangerous to the soundness of cement, especially at the later ages.

The customary method for expressing the relations is by means of ratios of the several oxides. Some of these values are based only on empirical results of experience, some on theoretical ideal composition in terms of the probable compounds formed. Ordinary or Portland cement, technically, is a greenish-grey active, impalpable powder made by burning to a high temperature in a rotary kiln, a pulverized mixture containing definite proportions of oxides of calcium, silicon, aluminum, and iron and grinding the resultant clinker. 2–6% gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) by weight (based on maximum limit of 2–2.5% of SO_3 in the cement) is added during grinding of clinker to control setting time.

Lime in cement has maximum limit. This can be expressed in terms of ratios of the oxides. In this instance, the molecular ratio of $\text{CaO}/\text{SiO}_2 < 3$, since the tricalcium silicate is the most basic of the silicates in cement, which can be seen from the following reaction of cement formation. Formation of cement take place by the reaction in the solid state to a great extent.



(cement resistant to sulphate-containing water should not contain $3\text{CaO}.\text{Al}_2\text{O}_3$ but only $4\text{CaO}.\text{Al}_2\text{O}_3.\text{Fe}_2\text{O}_3$).

When excess of lime is present, the compounds formed are $3\text{CaO}.\text{SiO}_2$ and $3\text{CaO}.\text{Al}_2\text{O}_3$, thus the upper limit for CaO is expressed by:

$$\frac{\text{CaO} + \text{MgO}}{\text{SiO}_2 + \text{Al}_2\text{O}_3} = 3.$$

If CaO decreases beyond a certain limit, $2\text{CaO}.\text{SiO}_2$ (dicalcium silicate) appears which disintegrates spontaneously and non-hydraulic. The lower limit for CaO (lime), in which tricalcium silicate ($3\text{CaO}.\text{SiO}_2$) will fail to appear is

$$\frac{\text{CaO} + \text{MgO}}{\text{SiO}_2 - (\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3)} = \text{not less than } 3.$$

If this ratio fails below 3, then the undesirable $2\text{CaO}.\text{Al}_2\text{O}_3$ will be formed. Experiments suggest that $3\text{CaO}.\text{SiO}_2$ and $2\text{CaO}.\text{Al}_2\text{O}_3$ is the best. But Portland clinker consists of tricalcium silicate ($3\text{CaO}.\text{SiO}_2$), and beta dicalcium silicate ($\beta\text{-}2\text{CaO}.\text{SiO}_2$) as principal constituents together with lesser and variable quantities of tricalcium aluminates ($3\text{CaO}.\text{Al}_2\text{O}_3$), tetra calcium alumino ferrite ($4\text{CaO}.\text{Al}_2\text{O}_3.\text{Fe}_2\text{O}_3$), or some solid solution of iron—phase, periclase (MgO), free lime (CaO), and trace amounts of many other compounds. Cement has to be hydraulic. This is expressed by the ratio of wt. percentage of their four major constituents (SiO_2 , Al_2O_3 , Fe_2O_3 , CaO).

$$\text{The hydraulic modulus (Hm)} = \frac{\text{CaO}}{\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3}.$$

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The hydraulic modulus should be between 1.8 and 2.2. When SiO_2 is too high, $(\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3)$ is decreased and the temperature of burning is raised, the influence of the lime is also lost. An expression for this is:

$$\text{the silicate modulus (Sm)} = \frac{\text{SiO}_2}{\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3} \quad (\% \text{wt..})$$

The value should be in the range of 2.0–2.5. Cement with high silicate modulus hardens slowly; that with low silicate modulus set rapidly.

12.1 SOLUTION PREPARATION AND APPARATUS/REAGENTS USED

150 ml beakers, stirrer, watch glass, white band filter paper, red band filter paper, conical flasks, funnel, porcelain (evaporating dish), crucible tong, grinding mortar, glass pistle, drying oven, igniting furnace, analytical balance, cooling desiccators, burette distilled water, heater (stove) measuring cylinders, and sand bath are used for the analysis.

Reagent Used

- HCl of $d = 1.19$ or 1.185
- AgNO_3 solution
- 10% Na_2CO_3 dissolving in 10% HCl
- 40% HF
- Cone H_2SO_4 of $d = 1.84$ 5% H_2SO_4
- HNO_3 of $d = 1.19$
- NH_4O_4 of 25%, 10%, 2.5%
- Na_2HPO_4 of 50%, 5%
- 3% NH_4NO_3
- Saturated $(\text{NH}_4)_2\text{C}_2\text{O}_4$, 0.1% $(\text{NH}_4)_2\text{C}_2\text{O}_4$
- 0.01% methyl orange solution
- 0.1N KMnO_4

Preparation of Reagent

Value of reagents in laboratory and value of reagents to be used are calculated by the formula:

$$C_1 d_1 V_1 = C_2 d_2 V_2.$$

1. HCl of 37%: $d = 1.185$, $N = 12.5$

HCl of 10%: $d = 1.0475$ is required to be prepared

$$V_1 = \frac{10 \times 1.0475 \times 50}{37 \times 1.185} = 11.9 = 12 \text{ ml}$$

12 ml of 37% is diluted with distilled water to 50 ml to give 10% HCl.

2. H_2SO_4 of 96%: $d = 1.84$, $N = 36$ is present in laboratory

H_2SO_4 of 5%: $d = 1.0325$ is required to be prepared.

$$V_1 = \frac{5 \times 1.0325 \times 200}{96 \times 1.84} = 5.845 = 5.85 \text{ ml}$$

5.85 ml of 96% is diluted with water to 200 ml to give 5% H_2SO_4

3. HNO_3 of 70.5%: $d = 1.4225$, $N = 16.14$

HNO_3 of 31.47%: $d = 1.19$ required to be prepared

$$V_1 = \frac{31.47 \times 1.19 \times 50}{70.5 \times 1.4225} = 18.67 = 19 \text{ ml}$$

19 ml of 70.5% is diluted with water to 50 ml to give $d = 1.19$ HNO_3 .

4. NH_4OH of 28%: $d = 0.898$, $N = 14.76$

(a) NH_4OH of = 25%: $d = 0.907$ is required to be prepared

$$V_1 = \frac{25 \times 0.907 \times 50}{28 \times 0.898} = 45 \text{ ml}$$

45 ml of 28% is diluted with water to 50 ml to give 25% NH_4OH .

(b) NH_4OH of 10%: $d = 0.957$ is required to be prepared

$$V_1 = \frac{10 \times 0.957 \times 200}{28 \times 0.898} = 76.12 = 76 \text{ ml}$$

76 ml of 28% is diluted with water to 200 ml to give 10% NH_4OH .

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(c) NH_4OH of 2.5%: $d = 0.987$ is required to be prepared

$$V_1 = \frac{2.5 \times 0.987 \times 50}{28 \times 0.898} = 4.9 = 5 \text{ ml}$$

5 ml of 28% is diluted with water to 50 ml to give 2.5% NH_4OH .

10% Na_2CO_3	10 g is dissolved with distilled water up to 10 ml
3% NH_4NO_3	3 g is dissolved with distilled water up to 10 ml
50% Na_2HPO_4	50 g is dissolved with distilled water up to 10 ml
5% Na_2HPO_4	5 g is dissolved with distilled water up to 10 ml
0.1% $(\text{NH}_4)_2\text{C}_2\text{O}_4$	0.1 g is dissolved with distilled water up to 10 ml
0.01% methyl orange	0.01 g is dissolved with distilled water up to 10 ml

- $(\text{NH}_4)_2\text{C}_2\text{O}_4$ is dissolved in water until it is saturated.
- 40% HF Solution is prepared
- 0.1N KMnO_4 is prepared by standardizing it with $\text{Na}_2\text{C}_2\text{O}_4$ as follows:

$$\text{KMnO}_4 = m = \frac{0.1 \times 31.6 \times 150}{1000} = 0.47415 \text{ g}$$

- 0.47415 g KMnO_4 is dissolved in water to 150 ml to give = 0.1 N

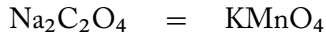
$$\text{Na}_2\text{C}_2\text{O}_4 = m = \frac{0.1 \times 67 \times 100}{1000} = 0.67 \text{ g}$$

- 0.67 g $\text{Na}_2\text{C}_2\text{O}_4$ is dissolved in water to 100 ml to give 0.1 N

$$\text{Na}_2\text{C}_2\text{O}_4 = m = 0.1 \times 67 \times 100 = 0.67 \text{ g}$$

- 0.67 g Na_2O_4 is dissolved in water to 100 ml to give 0.1 N
- The aliquant part (25 ml) of $\text{Na}_2\text{C}_2\text{O}_4$ is put into conical Flask and acidified with a small amount of HCl and tittered with KMnO_4 , until the apple (pink) color of KMnO_4 appears with one drop of it.
- Volume of KMnO_4 used for titration = 26 ml
- Volume of $\text{Na}_2\text{C}_2\text{O}_4$ taken for titration = 25.0 ml
- Normality of $\text{Na}_2\text{C}_2\text{O}_4 = 0.1 \text{ N}$

- Normality of $\text{KMnO}_4 = ?$



$$V_1N_1 = V_2N_2$$

$$0.25 \times 0.1 = 26.9 \times \times$$

$$N_{\text{KMnO}_4} = \frac{0.25 \times 0.1}{26.9} = 0.0929$$

$$26.9$$

12.2 SAMPLE ANALYSIS AND THEIR REPORT

12.2.1 EXPERIMENT NO. 1

Determination of Moisture Content

Procedure:

- 2.00 g of cement sample was weighed on analytical balance and put into reweighed crucible of known constant weight.
- Then it was dried in a drying oven at temperature of 110°C for 3 h.
- Next the crucible with content is put into a desiccator and cooled for 20 min and weighed.
- Again, it was dried for 1 h, then cooled and weighed.

Date obtained and calculation

1. Constant weight of crucible = 7.05800 g.
2. Wt. of crucible + cement sample = 9.05800 g.
3. Wt. of cement sample (b-a) = 2.00000 g.
4. Wt. of crucible + cement sample after drying for 3 h in 110°C = 9.03900 g.
After drying for 1 h = 9.03865 g.
5. Wt. of sample after drying (d-a)

$$9.03865 - 7.05800 = 1.98065 \text{ g.}$$

6. Wt. of moisture loss (c-e) = 0.01935 g.
7. Wt. of moisture loss in percentage

$$\frac{f \times 100}{C} = \frac{0.01935 \times 100}{2} = 0.9675\%.$$

12.2.2 EXPERIMENT NO. 2

Determination of Loss of Substance After Ignition

Procedure:

- 2.00 g of cement sample was put into crucible of known constant weight.
- Next it was dried in a drying oven for 30 min at 110°C and then ignited in the furnace at 1000°C for 1 h.
- Then it was cooled in a desiccator for 20 min and weighed.

Data obtained and calculation

1. Constant wt. of crucible = 6.90700 g.
2. Wt. of crucible + cement sample = 8.90700 g.
3. Wt. sample (b-a) = 2.00000 g.
4. Wt. of crucible + sample after drying for 30 min in the oven, and igniting it for 1 h in the furnace (d-a).

$$8.83700 - 6.90700 = 1.93000 \text{ g}$$

5. Wt. of substance lost (c-e).

$$2.00000 - 1.93000 = 0.07000 \text{ g}$$

6. Wt. of substance lost in percentage.

$$\frac{f \times 100}{C} = \frac{0.07000 \times 100}{2} = 3.5\%$$

*The substance lost are CO₂ and steam.

12.2.3 EXPERIMENT NO. 3

Determination of Undissolved Residue

Procedure:

1. 1 g of cement sample is put in a beaker of 150 ml and 25 ml of distilled water and 5 ml of concentrated HCl ($d = 1.185$) are added. By shaking the content, 50 ml of distilled water added. Then this mixture was heated for 15 min by covering the beaker with watch glass on a heater.

- The mixture was filtered on a white-band filter paper by using funnel. The precipitate was washed with cold water until chloride ions were removed (this was tested with AgNO_3) and after that the content of the filter paper was transferred to the beaker by washing it with a 30 ml hot 10% Na_2CO_3 solution.
- The content of the beaker was covered with watch glass and heated the necessary time for maximum moisture removal.
- Then the mixture was filtered on the filter paper and washed with hot distilled water. Then 10 drops of 10% HCl were added on the filter paper and it was washed until free from chloride ion with water (this was tested with AgNO_3).
- The filter paper with the residue was put inside a previously weighed crucible and ignited for 1 h at 1000°C in furnace then cooled in desiccators for 20 min and weighed.

Data obtained and calculation

- Wt. of crucible = 6.90700 g.
- Wt. of crucible + residue after ignition = 6.92045 g.
- Wt. of residue (b-c)

$$6.92045 - 6.90700 = 0.01345 \text{ g.}$$

- Wt. of undissolved residue in percentage

$$\frac{C \times 100}{\text{wt. of sample}} = \frac{0.01345 \times 100}{1.00000} = 1.345\%.$$

12.2.4 EXPERIMENT NO. 4

Determination of Silicic Acid as $\text{SiF}_4 \cdot (\text{SiO}_2 \cdot \text{SO}_3)$

Procedure:

- 0.4 g of cement sample is added into a 50 ml porcelain dish and to this 15 ml of distilled water and 10 ml HCl ($d = 1.185$) added.
- The mixture was evaporated on sand both until all the HCl disappears.
- Then the dry residue was treated with 10 ml of HCl ($d = 1.185$) and evaporated again.
- The content of the porcelain dish was grained with the glass pestle and collected toward the center of the dish and moistened with a few drops of HCl .

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- 30 ml of hot distilled water was added to the content and the mixture was heated for 10 m, and filtered on a red-band filter paper using funnel. Grains precipitate from the dish were transferred to the filter paper with the use of additional filter paper.
* The filtrate was saved for the next experiments.
- The precipitate was washed with hot distilled water until all the chloride ions are removed (this was checked with AgNO_3).
- The filter paper with precipitate was placed in a reweighed porcelain crucible and dried in an oven at 110°C for 30 min and ignited in the furnace for 3 h at 1000°C .
- Then it was cooled in desiccators for 20 min and weighed.
- The content was ignited, cooled, and weighed again until constant weight obtained.
* The weighed form was white in color.
- The content of the crucible was moistened with 2 ml of distilled water and 2 ml of 40% HF was added and evaporated under the hood.
- Then 1 ml of HCl was added and evaporated. Near the end of evaporation 2 ml of conc. H_2SO_4 ($d = 1.84$) was added and heating was continued till white fumes of SO_3 appear (this indicates that all the SiF_4 and HF have evaporated).
- Heating was continued until the white fume (SO_3) disappears.
- Then, after cooling the crucible with residue it was weighed.

Date obtained and calculation

- Wt. of crucible = 16.78900 g.
- Wt. of crucible + precipitate after ignition = 16.88000 g.
- Wt. of precipitate (b-a)

$$16.88000 - 16.78900 = 0.09100 \text{ g.}$$

- Wt. of the precipitate in percentage

$$\frac{C \times 100}{\text{wt. of sample}} = \frac{0.09100 \times 100}{0.4} = 22.75\%.$$

- Wt. of precipitate + crucible after treating with 40% HF and then after igniting = 16.87000 g.

6. Wt. of the evaporate (b–e)

$$16.88000 - 16.87000 = 0.00600 \text{ g.}$$

7. Wt. of evaporate in percentage

$$\frac{f \times 100}{\text{wt. of sample}} = \frac{0.00600 \times 100}{0.4} = 1.5\% \text{ SO}_3.$$

8. Percentage of SiO₂ (d–f)

$$22.75 - 1.5 = 21.25.$$

* The purpose of adding H₂SO₄ is to obtain SO₃ by oxidation which shows the complete evaporation of SiF₄ and HF by its appearance.

12.2.5 EXPERIMENT NO. 5

Determination of Iron and Alumina Oxides (R₂O₃)

Procedure:

1. The filtrate saved from determination of SiO₂ was heated in about a 200 ml beaker to boil.
2. Then, 0.5 ml of conc. HNO₃ ($d = 1.185$) and 4 drops of 0.01% methyl orange solution was added.
3. Finally, 10% NH₄OH solution was added drop by drop until the solution becomes slightly alkaline (orange in color).
4. Then the muddy solution was kept in hot place until the entire precipitates settle, and the liquid above the precipitate become transparent.
5. The precipitate was filtered on red-band filter paper and washed with 35% NH₄NO₃ solution until all the chloride ions are removed.

* The filtrate was saved for the next experiment.
6. The filter paper with the precipitate was transferred to a porcelain crucible and dried until it starts charring (in drying oven) and then ignited in a furnace at 1000°C for 1 h then cooled and weighed.

Data obtained and calculation:

1. Wt. of crucible = 6.90900 g.
2. Wt. of crucible + R₂O₃ after ignition = 6.94300 g.

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3. Wt. of R_2O_3 (b-a)

$$6.94300 - 6.90900 = 0.03400 \text{ g.}$$

4. % of

$$R_2O_3 = \frac{0.03400 \times 100}{0.4} = 8.5\%.$$

The average (%) proportions of $R_2O_3 = 9\%$. From this, 6.5% is Al_2O_3 and 2.5% is Fe_2O_3 . Therefore,

$$9 \text{---} 6.5 \quad \frac{8.5 \times 6.5}{9} = 6.138\% \quad Al_2O_3$$

$$8.5 \text{---} ?$$

$$9 - 6.138 = 2.362\% \quad Fe_2O_3 .$$

12.2.6 EXPERIMENT NO. 6

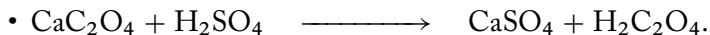
Determination of Calcium Ion

Procedure:

1. The filtrate which was saved from determination of R_2O_3 was acidified with few drops of HCl (pink color appears) and boiled.
2. 25 ml of hot saturated $(NH_4)_2C_2O_4$ solution was added, and 10% NH_4OH was added drop by drop until the solution became orange. The precipitate ($Ca_2C_2O_4$) is formed.
3. The solution was boiled until the precipitate settles and the mixture stood for 1 h undisturbed.
4. The precipitate was filtered with white-band filter paper and washed with hot 0.1% $(NH_4)_2C_2O_4$ solution at first until all the chloride ions are removed and then with hot water four times.
* The filtrate was saved for the next experiment.
5. The filter paper with the precipitate was carefully transferred to a 250 ml beaker, flattens it on the wall of the beaker and was poured 150 ml of hot 5% H_2SO_4 solution, gradually moving the filter paper outwards using a glass rod.
6. Then the solution was heated to $70^\circ C$ and titrated with 0.0929 N $KMnO_4$ solution.

NB No indicator was used for the titration because $KMnO_4$ has a pink color. One drop of $KMnO_4$ solution changes the colorless solution to pink at the equivalent point.

Data obtained and calculation



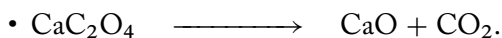
- Volume of solution ($\text{H}_2\text{C}_2\text{O}_4$) = 150 ml.
- Volume of KMnO_4 used for titration = 98.5 ml.
- Normality of KMnO_4 = 0.0929 N.

- Normality of $\text{H}_2\text{C}_2\text{O}_4$ = ?

$$\begin{array}{ccc} \text{KMnO}_4 & & \text{H}_2\text{C}_2\text{O}_4 \\ V_1 N_1 & & V_2 \times . \end{array}$$

- Normality of

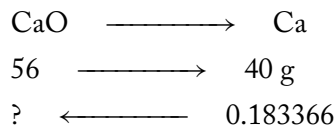
$$\text{H}_2\text{C}_2\text{O}_4 = \frac{98.5 \times 0.0929}{150} = 0.06100 \text{ N}$$



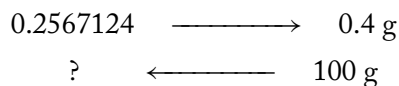
- Gm. eq. of Ca = 20.04 g.

- Wt. of

$$\text{Ca} = \frac{0.0610 \times 20.04 \times 150}{100} = 0.183366 \text{ g}$$



$$\frac{56 \times 0.183366}{40} = 0.2567124 \text{ g}$$



$$\% \text{CaO} = \frac{100 \times 0.2567124}{0.4} = \mathbf{64.1781\%}.$$

12.2.7 EXPERIMENT NO. 7

Determination of Magnesium Ion

Procedure:

1. The filtrate after removal of Ca^{++} ions was evaporated almost to dryness in a 250 ml beaker.

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2. After cooling the beaker, the residue was moistened with 3 ml HCl ($d = 1.185$) and 50 ml of distilled water was added and heated. The solution is pink.
3. The solution was acidified with HCl ($d = 1.19$) after adding 4 drops of methyl orange. The solution became light yellow in color.
4. 30 ml of 5% Na_2HPO_4 and 10% NH_4OH was added until the solution just turns alkaline (checked by litmus).
5. After cooling, the solution was diluted with 100 ml distilled water and 15 ml of 25% NH_4OH solution was added.
6. The precipitate waited for 3 h and then filtered through a white-band filter paper.
7. The precipitate was washed with 2.5% NH_4OH until all the Cl^- ions are removed.
8. The filter paper with precipitate was dried in drying oven with a previously weighed porcelain crucible and ignited in the furnace at 1000°C until the constant weight obtained.

Data obtained and calculation

1. Wt. of crucible = 6.90900 g.
2. Wt. of crucible + residue after ignition = 6.91955 g.
3. Wt. of residue (MgO) = $6.91955 - 6.90900 = 0.01055$ g.
4. % of

$$\text{MgO} = \frac{C \times 100}{\text{wt. of sample}} = \frac{0.01055 \times 100}{0.4} = \mathbf{2.6375\%}.$$

Other Calculations

1. The upper limit for CaO (lime)

$$\frac{\text{CaO} + \text{MgO}}{\text{SiO}_2 + \text{Al}_2\text{O}_3} = 3$$
$$\frac{64.1781 + 2.6375}{21.25 + 6.138} = \frac{66.8156}{27.388} = 2.4396.$$

2. The lower limit for CaO (lime)

$$\frac{\text{CaO} + \text{MgO}}{\text{SiO}_2 - (\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3)} = \text{not less than } 3$$
$$\frac{64.1781 + 2.6375}{21.25 - 8.5} = \frac{66.8156}{12.75} = \mathbf{5.2404}.$$

3. The hydraulic modulus

$$Hm = \frac{CaO}{SiO_2 + R_2O_3} = 1.8 - 2.2$$

$$\frac{64.1781}{21.25 + 8.5} = \frac{64.1781}{29.75} = \mathbf{2.1572}.$$

4. The silicate modulus

$$Sm = \frac{SiO_2}{R_2O_3} = 2.0 - - - 2.5$$

$$\frac{21.25}{8.5} = \mathbf{2.5}.$$

How do you grade this cement? Inferior, good, why?

The cement is graded as good quality because of the following.

1. The main composition of mineral oxides are found according to their proportion range in %

$$CaO = 64.178\% \quad SO_3 = 15\%$$

$$SiO_2 = 21.25\%$$

$$Al_2O_3 = 6.138\%$$

$$Fe_2O_3 = 2.3620\%$$

$$MgO = 2.6375\%$$

2. From the value of upper limit of CaO, we can see that excess of lime was not present, therefore, no possibility for expansion and cracking of mortar or concrete, and from the value of lower limit of CaO, we can see that there is no possibility of formation of undesirable $2CaO \cdot Al_2CaO \cdot SiO_2$.
3. From the hydraulic value range we can see that the cement has hydraulic property.
4. When SiO_2 is too high, $(Al_2O_3 + Fe_2O_3)$ is decreased and the temperature of burning is raised, the influence of high lime is also lost. Cement with high silicate modulus hardens slowly, that with low silicate modulus set rapidly. From the silicate modulus value we can see that, the value is in the required range.
5. From the content of MgO value we can see that there will be no possibility for soundness (decrease in volume) of cement at the early setting stage.
6. From all the chemical composition values we can see that the amount of gypsum added to control the setting time was a required amount.

12.3 CONCLUSION

From the theoretical expression, the cement production in any country must meet the good quality in order to carry out satisfactory construction work. As we can see from the sample analysis result, the cement which was produced in Ethiopia has good quality.

Since Ethiopia is a developing country, the demand of cement increases from time to time in every construction field. To fulfill this demand great work must be done in cement production and this must meet with modern technology and for this, skilled manpower is also very important.

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Author's Biography

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Tadele Assefa Aragaw is a lecturer in Chemistry and Environmental Engineering, a Researcher, and a Facility Manager in the Chemical and Food Engineering at the Bahir Dar Institute of Technology. Since 2017 he has been involved in a research project in the area of Ethiopian kaolin characterization for different industrial applications as well as an indigenous microalgae investigation from wastewater for biodiesel production.

In 2012, Tadele received his B.S. in Chemistry from the University of Gondar.

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