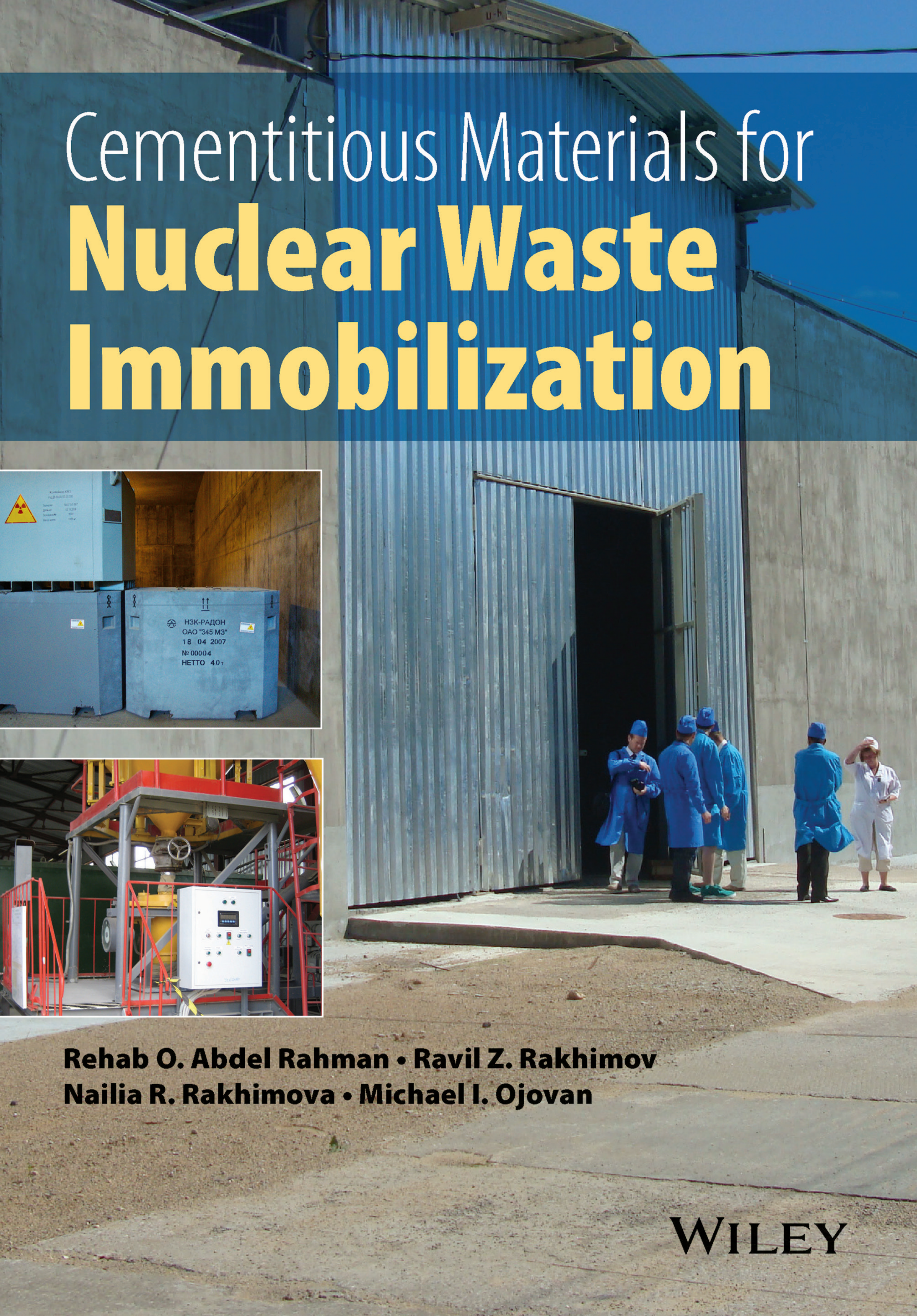
Cementitious Materials for Nuclear Waste Immobilization



Rehab O. Abdel Rahman • Ravil Z. Rakhimov
Nailia R. Rakhimova • Michael I. Ojovan

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PROFESSOR REHAB O. ABDEL RAHMAN

Hot Laboratory and Waste Management Centre,
Atomic Energy Authority of Egypt, Egypt

PROFESSOR RAVIL Z. RAKHIMOV

Kazan State University of Architecture and Engineering,
Russian Federation

PROFESSOR NAILIA R. RAKHIMOVA

Kazan State University of Architecture and Engineering,
Russian Federation

PROFESSOR MICHAEL I. OJOVAN

Imperial College London, UK

WILEY

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“To emeritus mathematician Vladimir Rolinskyi”.

Contents

About the Authors

Rehab O. Abdel Rahman is Associate Professor of Chemical Nuclear Engineering in the Radioactive Waste Management Department, Hot Laboratory and Waste Management Centre, Atomic Energy Authority of Egypt.

She received her PhD degree in Radioactive Waste Management from the Nuclear Engineering Department, Faculty of Engineering, Alexandria University, Egypt. Her research interests include different aspects of radioactive waste management, including radioactive waste treatment, conditioning and disposal. She has authored more than 25 peer-reviewed scientific papers and book chapters on radioactive waste management. She serves as a reviewer for some international journals, as Managing Editor for the *International Journal of Environment and Waste Management* and the *International Journal of Environmental Engineering* and was Editor of the book *Radioactive Waste* (InTech, 2012). She was awarded the State Incentive Award in Engineering Sciences, 2011 and selected as one of the 'Top 100 Engineers 2011' by the International Biographical Centre.

Ravil Z. Rakhimov is a Professor and Head of Department in the Department of Building Materials of the Kazan State University of Architecture and Engineering, Russian Federation.

He has been awarded DSc and PhD degrees in polymer research. He is a Fellow of the Russian Academies of Architecture and Building Sciences, Informatisation, and of Quality Problems, an Honoured Scientist of the Russian Federation, an Honorary Builder of the Russian Federation, and Laureate of the State Prize of the Government of the Russian Federation. He has authored over 600 scientific papers, has 32 patents, and published 39 monographs and textbooks on development and investigation of different mineral binders and building materials.

Nailia R. Rakhimova is a Professor in the Department of Building Materials of the Kazan State University of Architecture and Engineering, Russian Federation.

She has been awarded a DSc degree in alkali-activated slag-blended cements research and a PhD degree in polymer coatings research. She has authored over 100 scientific papers (in Russian) and 15 peer-reviewed scientific papers, has 6 patents, and published 1 monograph on alkali-activated slag cements and concretes.

Michael I. Ojovan has been Visiting Professor in the Department of Materials of Imperial College London and Associate Professor in the Department of Engineering Materials of the University of Sheffield. He is currently a Nuclear Engineer at the International Atomic Energy Agency Headquarters in Vienna, Austria.

He has been awarded a DSc degree in Physical Chemistry and a PhD degree in Solid State Physics. He is a Fellow of the Russian Academy of Natural Sciences and a Member of the Materials Research Society and International Commission on Glass. He has authored over 300 peer-reviewed scientific papers, has 42 patents, and published 11 monographs on nuclear materials including the second edition of *An Introduction to Nuclear Waste Immobilisation* (Elsevier, 2005, 2014). He is known for the two-exponential universal viscosity equation and the connectivity–percolation theory of glass–liquid transition.

Preface

Approaches and current practices of use of cementitious materials for nuclear waste immobilization are summarized in this book, with a focus on the most important aspects of cements as nuclear wasteforms. The topics covered include an introductory background on nuclear waste management, description of Portland cements and cements with mineral and chemical admixtures, alternative cementitious binders, radioactive waste cementation and equipment used, wasteform durability requirements and testing, and performance assessment.

Hydration of Portland cement as well as interaction of Portland cements with water and soil are described in detail. Also covered are mineral and chemical admixtures, chemical admixtures to control the structure and properties of Portland cements such as accelerators and retarders, plasticizers, and super-plasticizers, air-entraining agents, water-retaining agents and water permeability reducing admixtures, biocidal admixtures, mineral admixtures in the control of the composition, structure and properties of cements and mineral admixtures from natural rocks and minerals. Alternative binders are considered including calcium aluminate cements, calcium sulphoaluminate cements, phosphate cements such as magnesium and calcium phosphate cements, as well as alkali-activated cements. Cement properties relevant to waste immobilization are analysed including characterization and testing.

Radioactive waste streams suitable for cementation are described including both aqueous and organic waste, bulk and fragmented (dispersed) solid wastes as well as the description of cement-based wasteform optimization. Waste cementation technology and equipment are considered including methods of liquid and dispersed solid waste cementation and methods for cementation of bulk solid waste. Quality control of technological processes and materials obtained is discussed.

Cementitious wasteform durability requirements are examined along with the role of material performance and expected performance of cements. Wasteform leaching parameters and testing protocols such as IAEA/ISO 6961-82, ASTM C1220-98 (MCC-1), ANS-2009 (ANS/ANSI 16.1) and ASTM C1662-10 are given. Long-term field tests of cementitious materials are described as well as the effects of radiation, biological activities and role of filling materials. Performance assessment gives a brief overview of historical disposal practice, disposal facility design, modelling approaches, and safety case developed for disposal facilities.

Overall the book provides the reader with both a scientific and technological basis of using cementitious materials for immobilization of nuclear waste.

1

Introduction

1.1 Background of Nuclear Waste Problem

By definitions a waste is a material for which no further use is foreseen. For legal and regulatory purposes a radioactive (nuclear) waste is that waste which contains or is contaminated with radionuclides at concentrations or activities greater than clearance levels as established by the regulatory body. It is always recognized that this definition is purely for regulatory purposes, and that material with activity concentrations equal to or less than clearance levels is still radioactive from a physical viewpoint, although the associated radiological hazards are considered negligible [International Atomic Energy Agency (IAEA), 2003a]. Over recent years large amounts of radioactive waste have been generated during the production and application of radioactive materials both for peaceful and military purposes. The knowledge of the hazard associated with exposure to these wastes led to the adaptation of waste management strategies that relies on the concepts of containment and confinement. In radioactive waste repository, confinement may be provided by the wasteform and its container, whereas containment may be provided by the surrounding host rock (IAEA, 2013). The selection of the wasteform type and disposal option is determined based on the hazard imposed by the wastes. Although containment and confinement concepts have proven efficiency in isolating nuclear waste, there were some cases dating back to the early 1950s where radioactive wastes were disposed of unsolidified in unlined trenches. These practices led to radioactivity leaks in many sites, such as in Hanford, Washington, USA. The evaluation of the remediation costs and the hazard imposed from these practices on human health and the environment resulted in recognition of the need to have more rigorous confinement and containment strategies. This led to the development of new waste management systems which utilize volume reduction techniques and solidification/stabilization technologies to produce stable wasteforms and implement the multi-barrier disposal concept to ensure safe disposal of these wastes.

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Currently safe management of nuclear wastes is a subject that is receiving considerable attention from public and different governmental, regional and international bodies. This recognition has not only stemmed from the huge volume of the cumulative wastes and the diversity of their chemical, biological and radiological hazards but also because the public relates their acceptance for new nuclear power programmes to their confidence in the waste management practice (Abdel Rahman, 2012). In the following sections, the facilities that generate nuclear wastes will be briefly introduced, different waste classification schemes and waste management activities will be presented and matrix material for nuclear waste immobilization will be highlighted.

1.2 Nuclear Industry Facilities

The nuclear fuel cycle (NFC) and radioisotope production and application facilities are considered the main generators for nuclear wastes. The NFC includes all operations associated with the production of nuclear energy, namely mining and milling, processing and enrichment of uranium or thorium; manufacture of nuclear fuel; operation of nuclear reactors (including research reactors); reprocessing of nuclear fuel; any related research and development activities and all related waste management activities (including decommissioning). During the lifecycle activities of these facilities, different amounts of wastes with varying characteristics are produced. Within the operational and decommissioning phases only nuclear wastes are generated whereas other phases produce non-nuclear wastes, for example soils from excavation, building materials and so on. Nuclear wastes produced within the operational phase are usually characterized by their limited amounts; on the other hand, a much larger volume of waste is generated during the decommissioning phase (IAEA, 2007). This section will introduce operational processes that take place in different nuclear facilities and lead to generation of radioactive wastes, whereas the wastes generated during the decommissioning phase of these facilities will be discussed in Chapter 6.

1.2.1 NFC Facilities

The NFC refers to activities associated with the production of electricity using nuclear reactors (IAEA, 2003a). They are classified based on the existence of recycling option into two categories, namely open and closed NFCs, as illustrated in Figure 1.1 (Ojovan and Lee, 2005). Facilities that operate from nuclear ore extraction to fuel loading into a nuclear reactor are known as front-end NFC facilities; these include mines, mills, fuel enrichment and fuel fabrication facilities. After using the fuel in the reactor, the facilities that deal with used (spent) fuel and radioactive waste are referred to as back-end NFC facilities; they include fuel storage and/or fuel reprocessing plants. The operation of each facility is associated with the generation of different types of nuclear wastes. It is worth mentioning that nuclear materials generally can pose chemical, radiological and flammability hazards. Accordingly, there is a need to specify these hazards and implement certain safety measures to counter these hazards. Table 1.1 lists the safety aspects associated with the hazard of nuclear wastes at NFC facilities (IAEA, 2005a).

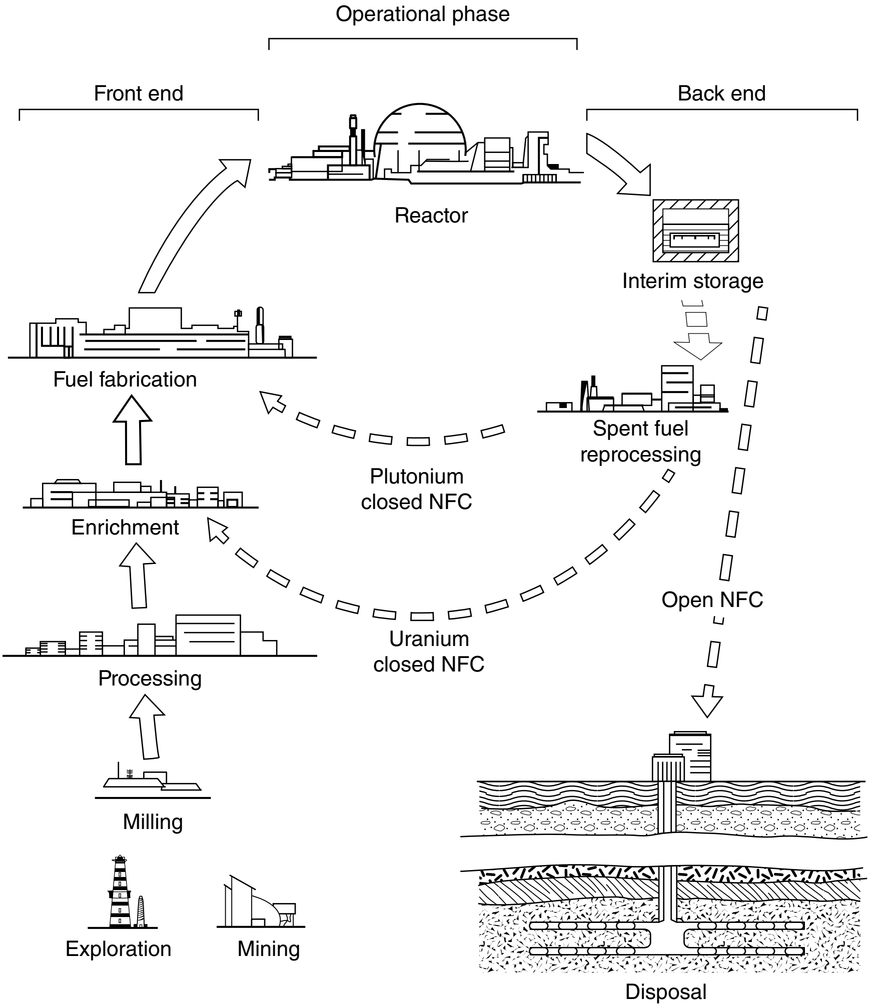

Figure 1.1 *Open and closed NFCs. Reproduced with permission from Ojovan and Lee, 2005. © 2005, Elsevier*

1.2.1.1 Mining and Milling Facilities

Mining uranium ore is the first step in any NFC, where uranium is extracted from a mine and then concentrated in a mill. The uranium mill is usually located near the mine to reduce shipping charges. The concentration processes involved include crushing, grinding, leaching, precipitation, solvent extraction and ion exchange (Benedict *et al.*, 1981). The concentrate is composed of uranyl nitrate solution, $[UO_2(NO_3)_2]$, and solid ammonium diuranate, $[(NH_4)_2U_2O_7]$, which is known as yellow cake. The operation of these facilities generates large amounts of solid wastes in the form of natural materials, that is displaced soil, and radioactive contaminated tailings. The radioactivity content in tailings is above the background level; usually they are returned to the pit from where the uranium ore was

Table 1.1 *Hazard identification at different NFC facilities*

Facility	Criticality	Radiation	Chemical toxicity	Flammability
Mining/milling	—	XX	XX	X
Conversion	X	XX	XX	XX
Enrichment	X	XX	XX	XX
Fuel fabrication	XX	XX	XX	XX
Reprocessing	XX	XX	XX	XX
Storage	XX	XX	—	—
Transportation	X	XX	X	XX

X, hazard may be of concern; XX, hazard of concern.

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originally extracted and the site rehabilitated for further use (see Section 6.4). In some cases this operation is not economically feasible, so the tailings are stored then transported to a long-term stable structure and the site is rehabilitated for further use (Alexander and McKinley, 2007). Also, large volumes of effluent are generated during the operation of mines and mills; historically these effluents were held in storage ponds and eventually evaporated to solids (Benedict *et al.*, 1981). Currently the treatment of these effluents and their control is becoming a concern because of the strengthened regulatory requirements. The main problems that arise when dealing with these effluents are due to their large volumes and the nature of contaminants where both radioactive and non-radioactive toxicants exist (IAEA, 2004).

1.2.1.2 Uranium Refining Facilities

Refining uranium concentrate is performed by purifying the concentrate, where chemical impurities are removed, followed by conversion of purified concentrate into a suitable chemical form. The purification is conducted by dissolving the concentrate in nitric acid and then applying solvent extraction to remove impurities. Purified concentrate is then converted to uranium trioxide (UO_3) or uranium dioxide (UO_2), depending on the type of reactor. To produce UO_3, either thermal denitration (TDN) or ammonium diuranate (ADU) could be used, where ammonium uranyl carbonate (AUC) is used to obtain UO_2. TDN is a one-step process from which fine UO_3 powder is produced. With ADU and AUC, the purified uranium is subjected to precipitation, filtration and calcinations/calcinations with hydrogen; Figure 1.2 illustrates these processes. The wastes arising from refining processes are mainly generated during the purification step. They include liquid effluent sludge, insoluble and filter aid, and drums (IAEA, 1999a).

If enrichment is required, UO_3 will be transformed to uranium hexafluoride (UF_6) according to the following reaction:

$$UO_3 \xrightarrow{H_2} UO_2 \xrightarrow{HF} UF_4 \xrightarrow{F_2} UF_6 \tag{1.1}$$

Figure 1.3 illustrates the sequence of the chemical process to produce UF_6; these chemical processes generate wastes in the form of solid calcium fluoride, calcium hydroxide, water

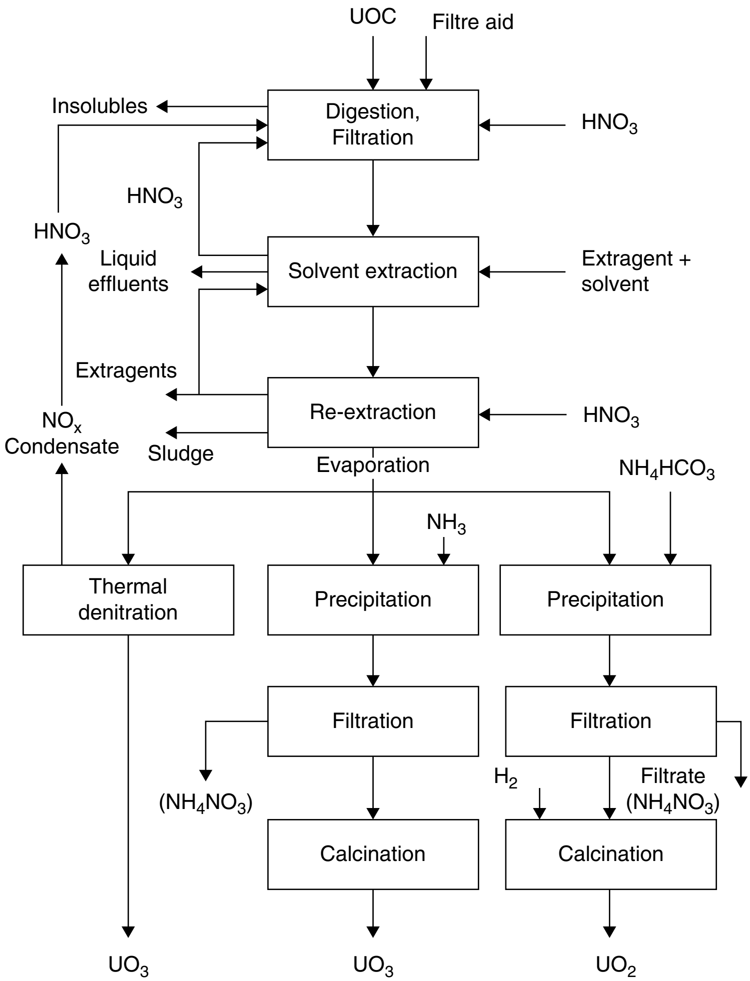

Figure 1.2 *Flowchart for the production of uranium trioxide and uranium dioxide. Reproduced with permission from IAEA, 1999a. © 1999, IAEA*

contaminated by uranium and gaseous wastes that contain UF_6, F_2 and HF (IAEA, 1999a, 2008). UF_6 is then directed to the enrichment plant to increase the percentage of uranium fissionable isotope (^{235}U) to the required ratio depending on the reactor type. There are several technologies available for enriching uranium; these include electromagnetic isotope separation, thermal diffusion, aerodynamic uranium enrichment process, chemical exchange isotope separation, ion exchange process, the plasma separation process, gaseous diffusion process, gas centrifuge process and laser isotope separation. Gas diffusion and gas centrifuge are considered the most widely used commercial methods (IAEA, 2005a). The enrichment process generate wastes in the form of depleted UF_6, which can be converted to stable, insoluble and non-corrosive U_3O_8 that can be safely stored pending reuse (IAEA, 2009a).

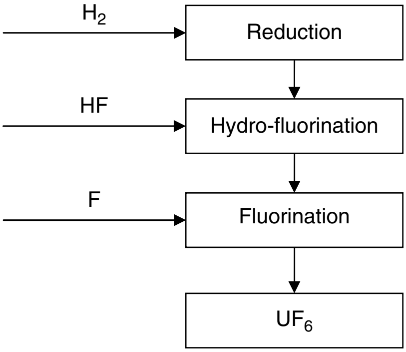

Figure 1.3 *Sequence of the chemical process to produce UF_6. Reproduced with permission from IAEA, 2008. © 2008, IAEA*

In commercial light-water nuclear power reactors (pressurized water and boiling water reactors), the fuel is formed of UO_2, so UF_6 is converted to UO_2. The integrated dry route method is one of the methods that is commonly used for this purpose, where UF_6 vapour is reacted with a mixture of superheated dry steam and hydrogen at ~600–700 °C as follows:

$$UF_6 + 2H_2O + H_2 \xrightarrow{600-700^\circ C} UO_2 + 6HF \qquad (1.2)$$

The process does not generate any liquid effluent but by-product wastes in the form of high purity HF, which could be recovered and reutilized (IAEA, 2005a). UO_2 powder is then granulated and subjected to high temperature sintering to produce fuel pellets. Uranium pellets are then loaded into the clad to form fuel rod and then attached together in arrays to form a fuel assembly. The assembly shape is designed to meet the neutronic and thermal–hydraulic characteristics of the reactor and to provide the first level of containment for fission products and actinides that are generated during the irradiation of nuclear fuel. Figure 1.4 shows different processes to produce UO_2 nuclear fuel pellets (IAEA, 1999a). It is worth mentioning that for other reactors the amount and type of wastes that are generated during fuel fabrication is markedly different.

1.2.1.3 Nuclear Reactors

Nuclear reactors are used to irradiate nuclear fuel to release energy; there are different types of reactors. Table 1.2 presents a comparison between different reactor types and their configuration (IAEA, 2009a). The fuel service life time depends on the characteristics of the reactor, initial composition of the fuel, neutron flux to which it is exposed and the way in which the fuel is managed in the reactor. Factors that eventually require fuel to be discharged include deterioration of cladding as a result of fuel swelling, thermal stresses or corrosion, and loss of nuclear reactivity as a result of depletion of fissile material and build-up of neutron-absorbing fission products. A typical fuel service life time is 3 years.

The normal operation of nuclear reactors is associated with the generation of different nuclear wastes in the form of effluent associated with decontamination activities of the primary coolant, lubricants, wet storage and detergent wastes. Wet solid wastes are also

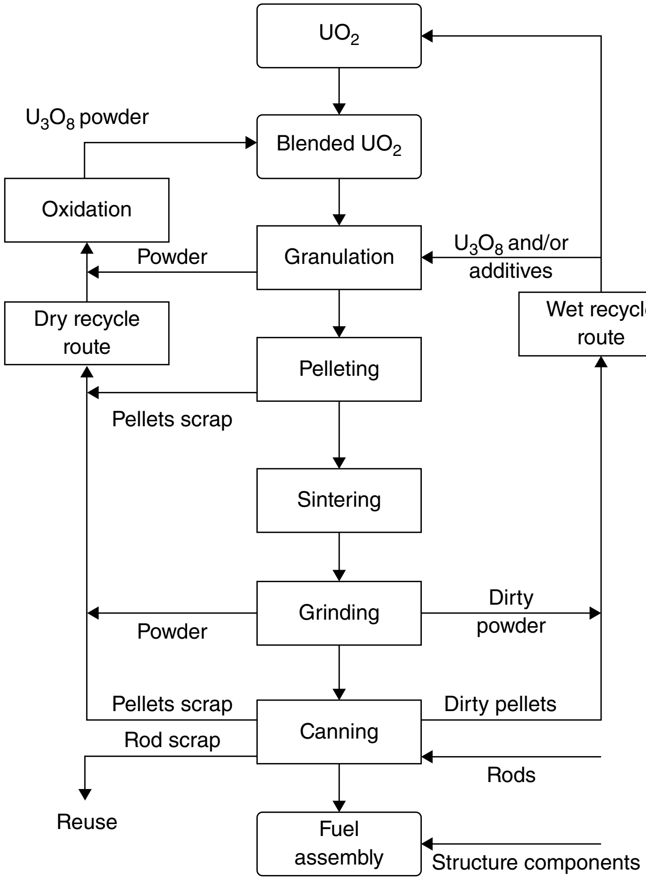

Figure 1.4 *Light water reactor fuel pellet manufacturing flow diagram. Reproduced with permission from IAEA, 1999a. © 1999, IAEA*

produced in the form of ion-exchange resins and sludge and dry waste solids, i.e. rubber gloves and paper tissue.

1.2.1.4 Repossessing Plants and Storage

When spent fuel is discharged from the reactor, it contains substantial amounts of fissile and fertile materials. In an open NFC, the spent fuel is cooled in a storage basin (wet storage) to allow for heat intensity decrease and short-lived radioactivity decay and is then transported to dry storage. In a closed NFC, the spent fuel is shipped in strong and heavily shielded casks that are capable of withstanding damage during a shipping accident to a reprocessing plant where decladding is performed to remove the clad either chemically or mechanically. During decladding, the fuel rod is dissolved in acid, and fissile and fertile materials are separated from fission products and from each other. Different chemical processes are commercially available; PUREX(plutonium, uranium, reduction, extraction) is one of these processes. Plutonium and uranium are considered the most valuable materials to be recovered. This process utilizes the separated fission products to obtain relatively pure plutonium and

Table 1.2 Configuration of different reactor types

Reactor type	PWR/ WWER	BWR	PHWR	RBMK	AGR	MAGNOX	FR
Neutron spectrum	Thermal	Thermal	Thermal	Thermal	Thermal	Thermal	Fast
Moderator	H_2O	H_2O	D_2O	Graphite	Graphite	Graphite	–
Coolant:							
type	Press. H_2O	Boiling H_2O	Pr. D_2O	Boil. H_2O	CO_2	CO_2	Na
Pressure, bar	155	70	110	70	40	19	5
temperature, outlet, °C	320	286	310	284	630	400	550
Fuel:							
type	UO_2 or MOX	UO_2 or MOX	UO_2	UO_2	UO_2	U metal	UO_2^*
enrichment	up to 5% ^{235}U eff.	up to 5% ^{235}U eff.	Nat. U	up to 3% ^{235}U eff.	2.5–3.8% ^{235}U eff.	Nat. U	17–26% ^{235}U*
Cladding	Zr alloy	Zr alloy	Zr alloy	Zr alloy	SS**	MgO-Al	SS**
Burnup, GWD/t HM	Up to 60	Up to 55	7	Up to 25	Up to 30	4	Up to 100*
Number of operating reactors	229	93	39	16	14	8	1
Total power, GWe	240.6	82.6	20	11.4	8.4	2.3	0.6*

*data for Russian BN-600
**SS–stainless steel
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uranium nitrates and nuclear wastes are generated as by-product. This process includes five phases, namely preparation for dissolution, fuel dissolution, feed preparation, primary decontamination and uranium and plutonium separation. The last phase includes four activities, that is solvent extraction, organic phase recycling, diluents wash and nuclear waste management. The solvent extraction activity utilizes tributyl phosphate diluted using organic diluents. Diluents are used to maintain the viscosity and density of the organic phase in the workable range. Figure 1.5 illustrates the sequence of activities to separate uranium and plutonium using the PUREX method. Plutonium in nitrate form is usually converted to oxide or carbide and used in fuel for fast reactors or recycled to thermal reactors, where uranium nitrate is converted to UF_6. Other valuable isotopes that have medical or industrial uses such as ^{137}Cs may also be recovered and the rest of the fission products are considered as waste effluent that needs to be safely managed (IAEA, 2009a).

1.2.2 Radioisotope Production and Application

Radioisotopes have a large number of applications in different fields where isotopes are produced in research reactors or in particle accelerators. The operation of particle accelerators is associated with radioactive waste production in the course of activated parts removal

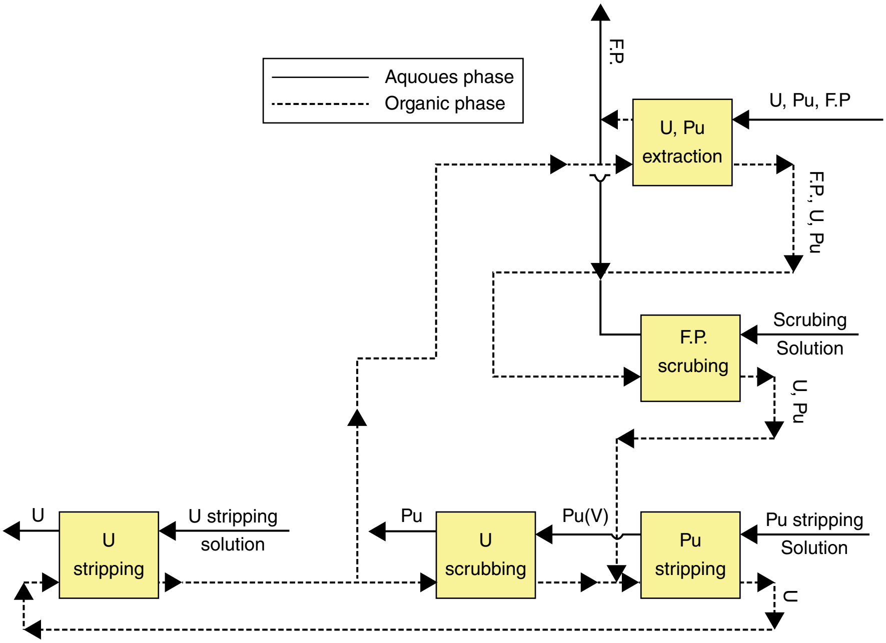

Figure 1.5 *Separation of uranium and plutonium using the PUREX method*

or replacement or as a result of neutron activation of materials. The waste generated from the latter is characterized by its relatively short-lived radionuclide content and small amount. Some accelerator-based neutron generators use large tritium targets which become tritium contaminated waste (IAEA, 2003b). If research reactors are used to produce the isotopes, the operation of the reactor will generate wastes in the form of organic and aqueous effluents and wet and dry solid waste as discussed earlier. The produced isotopes are extracted or processed in hot cells or laboratories. Most of the wastes produced from this step contain a mixture of long- and short-lived radionuclides. Long-lived fission products and/or transuranic radionuclides are not usually generated in the laboratories of small nuclear research centres. Only a small part of the radioactive waste from these centres is contaminated with long-lived radioisotopes, that is ^{14}C and ^{3}H (IAEA, 2001a).

Liquid radioactive solutions, sealed and unsealed sources of high to low concentrations, are used during normal operation of facilities using radioisotope applications. The quantities and types of the generated wastes are largely dependent on the application. In medicine, radioisotopes are used for radio-immunoassays, as radiopharmaceuticals, for diagnostic procedures, for radiotherapy, for sterilization and for research (Abdel Rahman *et al.*, 2014). These isotopes are characterized by their very short life, and in most cases the only operation performed on the waste is the storage for decay before further treatment to eliminate biological hazards and/or release to the environment. In industry, the radioisotopes are used to perform quality control, measure level and thickness, check the performance of equipment and improve its efficiency. In universities and research establishments, labelled compounds are widely used; these compounds have typically low radioactivity content.

1.3 Nuclear Waste Sources and Classification

Classification systems are used to ease the management of certain waste type. The development of these systems is usually performed to support planning and designing waste management strategies and facilities, define the operational activities and facilitate record keeping and communications (IAEA, 1970). Nuclear wastes may be classified based on safety and/or regulatory criteria, waste characteristics, or process engineering. This led to the evolution of different classification systems in different facilities and a variety of terminologies that differ from country to country. In this section different classifications based on activity limit will be overviewed; classification based on the physical and chemical characteristics of the waste and their different types will be discussed in Chapter 6.

The radioactivity level in the waste affects the selection of its different management options owing to its shielding requirements. The IAEA have recommended a classification system based on the activity level and half-life of the main pollutant in the waste stream (IAEA, 1999b). This system classifies the radioactive wastes into four classes, namely exempt waste (EW), low- and intermediate-level waste (LILW), which may be subdivided into short-lived low- and intermediate-level waste (LILW-SL) and long-lived low- and intermediate-level waste (LILW-LL) and high-level waste (HLW). Table 1.3 lists the characteristics of these waste classes (IAEA, 1970, 1994a, 1999b; Abdel Rahman *et al.*, 2011a).

In this classification there was not a direct link between the waste classes and the disposal options which limited its use and application (IAEA, 2009b; Ojovan, 2011). To address this shortcoming and to reflect the progress made in disposal safety, the IAEA defined six waste classes with general boundary conditions. These classes are EW, very short-lived waste (VSLW), very low-level waste (VLLW), low-level waste (LLW), intermediate-level waste (ILW) and HLW. Table 1.4 lists these classes; it can be noted that the definition of EW has been retained from the previous classification. Figure 1.6 illustrates the relationship between the half-life and radioactivity content for each class and their corresponding disposal option (IAEA, 2009b).

Table 1.3 *IAEA radioactive waste classification system*

Waste classes	Typical characteristics
EW	Activity levels at or below clearance levels, which are based on an annual dose to members of the public of <0.01 mSv
LILW	Activity levels above clearance levels and thermal power[a] <2 kW/m^3
LILW-SL	Restricted long-lived radionuclide concentrations (limitation of long-lived alpha-emitting radionuclides to 4000 Bq/g in individual waste packages and to an overall average of 400 Bq/g per waste package)
LILW-LL	Long-lived radionuclide concentrations exceeding limitations for short-lived waste
HLW	Thermal power >2 kW/m^3 and long-lived radionuclide concentrations exceeding limitations for short-lived waste

[a] This figure is unrealistically high and most probably was due to a misprint which has wrongly indicated kW/m^3 instead of W/m^3. Fortunately it has not been used in practice as it could cause overheating of waste tanks at volumes of 10 m^3. The current IAEA classification scheme (Table 1.4) has replaced that figure emphasizing that management of decay heat should be considered in a disposal facility if the thermal power of waste packages reaches a few watts per cubic metre (IAEA, 2009b).

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Table 1.4 *Current IAEA radioactive waste classification system*

Waste classes	Typical characteristics
EW	Waste that meets the criteria for clearance, exemption or exclusion from regulatory control for radiation protection purposes
VSLW	Waste that can be stored for decay over a limited period of up to a few years and subsequently cleared from regulatory control
VLLW	Activity levels above clearance levels, but does not need high level of containment; it can be disposed in near surface with limited regulatory control. The concentrations of longer-lived radionuclides are very limited
LLW	Activity levels above clearance levels with limited amount of long-lived radionuclides. It requires robust isolation and containment for periods of up to a few hundred years and is suitable for disposal in engineered near surface facilities
ILW	Long-lived radionuclide concentrations, in particular, alpha-emitting radionuclides that will not decay to a level of activity concentration acceptable for near surface disposal during institutional controls period. ILW also includes waste that needs no provision, or only limited provision, for heat dissipation during its storage and disposal
HLW	Its activity concentration is high enough to generate significant quantities of heat or wastes with large amounts of long-lived radionuclides

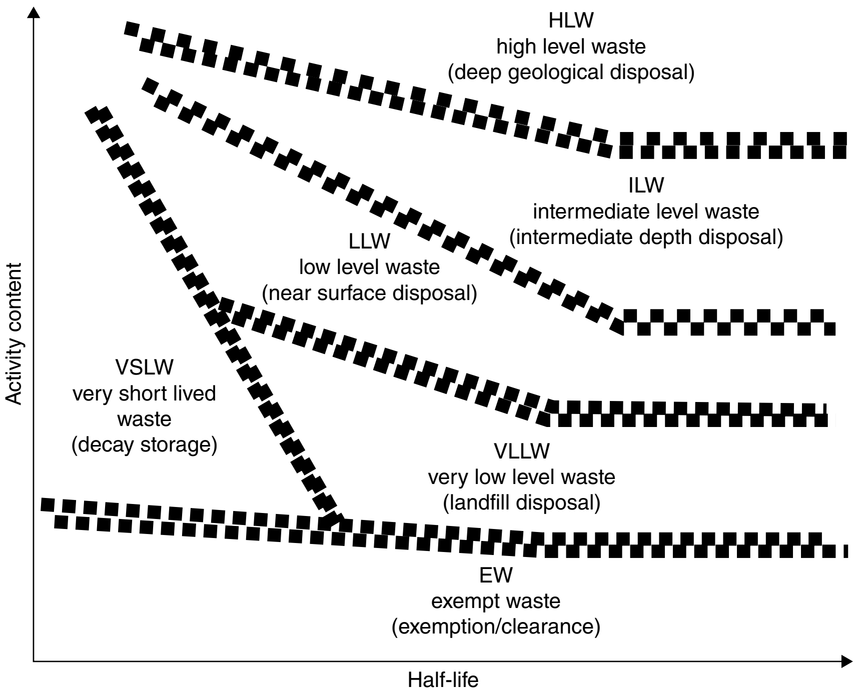

Figure 1.6 *New IAEA waste classification system. Reproduced from IAEA, 2009a. © 2009, IAEA*

Table 1.5 *NRC waste classification systems (NRC, 2013)*

Long-lived radionuclides	Concentration (Ci/m^3)	Short lived	Maximum concentration (Ci/m^3)		
			A	B	C
^{14}C	8	^{137}Cs	1	44	4600
^{14}C[a]	80	^{3}H	40	[b]	[b]
^{59}Ni[a]	220	^{60}Co	700	[b]	[b]
^{94}Nb[a]	0.2	^{63}Ni	3.5	70	700
^{99}Tc	3	^{63}Ni[a]	35	700	7000
^{129}I	0.08	^{90}Sr	0.04	150	7000
Alpha emitting transuranic nuclides >5 y half-life	100[c]	Nuclides total <5 y half-life	700	[b]	[b]
^{241}Pu	3500[c]				
^{242}Cm	20 000[c]				

[a] In activated metal.
[b] No limit for these classes.
[c] Units are nCi/g. 1 Ci = 3.7×10^{10} Bq (disintegrations/s).

Table 1.6 *UK classification system*

Waste classes	Typical characteristics
VLLW, low volume	Wastes which can be disposed of with ordinary refuse, each 0.1 m^3 of material containing less than 400 kBq of beta/gamma activity and is mostly comprised of small volumes from hospitals and universities. For carbon-14 and tritium containing wastes, the activity limit is 4000 kBq for each 0.1 m^3 in total
VLLW, high volume	Radioactive waste with an upper limit of 4 MBq per tonne (not including tritium) that can be disposed to specified landfill sites. For tritium containing wastes, the upper limit is 40 MBq per tonne
LLW	Containing radioactive materials other than those suitable for disposal with ordinary refuse, but not exceeding 4 GBq per tonne of alpha or 12 GBq per tonne of beta/gamma activity
ILW	Wastes with radioactivity levels exceeding the upper boundaries for LLW, but which do not need heating to be taken into account in the design of storage or disposal facilities
HLW	Wastes in which the temperature may rise significantly as a result of their radioactivity, so this factor has to be taken into account in designing storage or disposal facilities

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Although many countries have applied the IAEA recommended radioactive waste classification system, there are others that utilize their own classification schemes. The National Regulatory Commission(NRC) of the USA developed a waste classification system based on the concentration of short- and long-lived radionuclides and their shorter-lived precursors which was initiated to support the disposal decision of either near surface disposal or storage

Table 1.7 *Practical classification of radioactive waste in Russia*

Category of waste	Specific radioactivity (Bq/g)			
	Tritium	Beta radionuclides (except tritium)	Alpha radionuclides (except transuranic)	Transuranic radionuclides
Low level	From 10^6 to 10^7	$<10^3$	$<10^2$	<10
Intermediate level	From 10^7 to 10^{11}	From 10^3 to 10^7	From 10^2 to 10^6	From 10 to 10^5
High level	Over 10^{11}	Over 10^7	Over 10^6	Over 10^5

Table 1.8 *French classification system*

Waste classes	Disposal option
VLLW	Short-lived VLLW is managed using storage for decay, then disposed in conventional waste disposal (<100 day) Long-lived VLLW is disposed in CSTFA disposal facility
Tritium-containing wastes	Storage before disposal to allow for tritium decay
LLW	Short-lived LLW disposed at CSFMA disposal facility (<31 year) Long-lived LLW disposed in near surface disposal (15–200 m deep)
ILW	Short-lived LLW disposed at CSFMA disposal facility (<31 year) Long-lived ILW disposed in deep disposal (500 m deep)
HLW	Disposed in deep disposal (500 m deep)

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until geological disposal is available (NRC, 2013). Waste classes are labelled alphabetically, for example A-class waste has the least requirements for disposal. Table 1.5 lists the potential short- and long-lived radionuclides and their corresponding maximum concentrations.

The radioactive waste classification scheme in the UK, as illustrated in Table 1.6, categorizes the wastes into VLLW, LLW, ILW and HLW (Ojovan and Lee, 2014).

Another classification based on waste activity is applied in Russia where the wastes are classified based on the specific activity of the radionuclides, as indicated in Table 1.7 (Ojovan and Lee, 2005, 2014).

The French classification system utilizes the activity level and half-life of the waste to specify the disposal option (ANDRA, 2013) (Table 1.8).

1.4 Nuclear Waste Management

In order to achieve safe containment and confinement of radioactive waste, the waste management system is currently designed to reduce the waste volume by using different volume reduction techniques that vary depending on the chemical, physical, biological and radiological characteristics of the waste so a stable wasteform is produced (IAEA, 1992, 2002a). Volume reduction, immobilization, storage, transportation and disposal processes are considered as elements of the radioactive waste management system. It should be noted that for every nuclear activity there should be a waste minimization

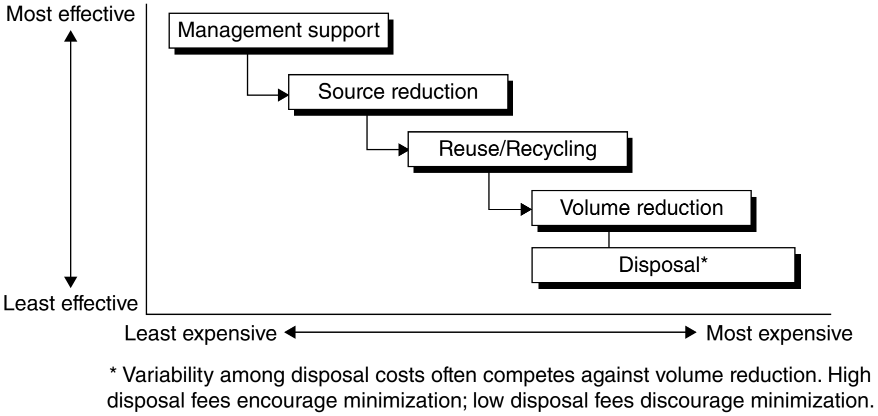


Figure 1.7 *Basic concept included in low- and intermediate-level wastes. Reproduced with permission from IAEA, 2006. © 2006, IAEA*

programme that aims to reduce the amount of generated wastes. Such programmes should cover the organizational, technological and economic aspects of the performed waste minimization processes. The key considerations of the minimization programme are illustrated in Figure 1.7. Management support is achieved by assigning the minimization programme as one of the facility's performance indicators. Different source reduction strategies should be adopted and implemented from the planning phase of the plant to the decommissioning phase. Finally, the waste should be subjected to volume reduction before being disposed (IAEA, 2006). The presentation of control on contamination spread is one of the activities conducted in the minimization programme.

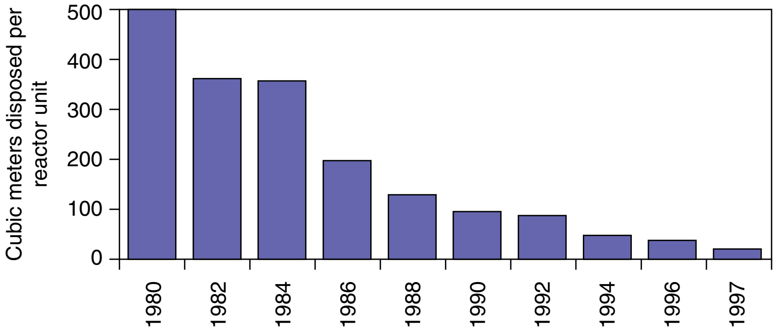
Finally, the selection of the treatment processes and the chemicals utilized may help in avoiding the production of chemically toxic radioactive wastes (Abdel Rahman, 2012).

The application of the waste minimization programmes in different countries has led to a considerable reduction in the final volume of disposed wastes. Figure 1.8 illustrates the reduction in the disposed waste volume that resulted from application of minimization programmes in the USA (IAEA, 2001b). As shown in the figure, waste generation has reduced drastically since 1996 when the minimization programme started.

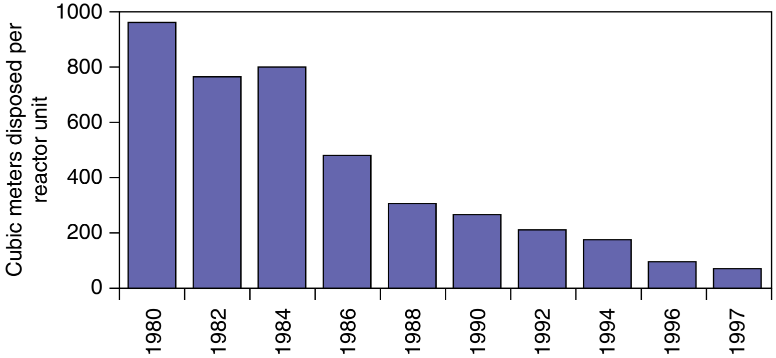
To achieve the overall safety goal of waste management, these elements must be complementary and compatible with each other (Abdel Rahman *et al.*, 2005). Before planning such a system, a clear policy statement should be identified and then during the system being established, the management strategy and legal framework should be developed. In this section the development of nuclear waste policy principles, strategy and legal framework will be introduced and technical options for the elements of the waste management system will be briefly considered. Finally, factors that affect the technology selection will be discussed.

1.4.1 Development of Policy Principles, Strategy and Legal Framework

Protecting human health and the environment now and in the future from the hazard associated with exposure to nuclear wastes are the ethical and environmental policy principles that were suggested by the IAEA to support the sustainability of the environment and the safe



Waste minimization for PWR reactors
in the United States of America



Waste minimization for BWR reactors
in the United States of America

Figure 1.8 *Results of the waste minimization programme in the USA: (a) for pressurized water reactors; and (b) for boiling water reactors. Reproduced with permission from IAEA, 2001b. © 2001, IAEA*

management and disposal of nuclear wastes (IAEA, 1995). These principles are applicable to all types of radioactive wastes, regardless of their physical and chemical characteristics or origin. In addition, each country has its own policy principles that reflect the national priorities, circumstances, structures and human and financial resources. The aim of developing these principles is to define the goals and requirements for the legislative framework, also these principles might include administrative and operational measures (Abdel Rahman, 2012: Abdel Rahman *et al.*, 2011b). To support the efforts in many countries to develop or update their national policy principles, the IAEA have issued guidelines to develop such principles (IAEA, 2009c).

Assignment of responsibility, identification of available information and evaluation of possible endpoints and technical options are the main steps in developing a national strategy. To support the implementation of the policy principles there is a need to establish a legal framework. That framework should be a part of the national legal system and has a hierarchical structure usually starting at the constitutional level and ending with regulations for authorization, assessment, inspection and enforcement. In some countries another level is added that identifies

Table 1.9 Treatment options for liquid nuclear waste streams

Aqueous wastes		Organic wastes
Method	DF	
Chemical precipitation	10–100	Incineration
Ion exchange	$>10^4$	Wet oxidation
Evaporation	10^4–10^6	Electrochemical oxidation
Reverses osmosis	100–1000	Acid digestion
Filtration (ultra and micro)	Up to 99%	Biological digestion
Solvent extraction	—	Emulsification

DF, decontamination factor.

non-mandatory guidance instruments which contain recommendations designed to assist people and organizations in meeting the legal requirements (IAEA, 2009c; Abdel Rahman, 2012).

1.4.2 Technical Options for a Waste Management System

Treatment, immobilization, transportation, storage and disposal are the main elements of any nuclear waste management system; treatment includes operations that change the waste characteristics to enhance the safety and economic aspects of the waste management system. There are different treatment options that are commercially available for the treatment of radioactive wastes. The selection of the appropriate technology is restrained by many technical aspects; the most important are the physical, chemical and radiological characteristics of the wastes. Generally treatment relies on reduction of the volume of generated waste. The treatment of aqueous waste aims to divide the waste stream into two portions: the first has large volume and its activity content meets the regulatory requirement for release; and the second has a small volume that contains nearly all the radioactivity. The decontamination factor is a parameter that is used to evaluate the performance of the treatment process; it is defined as the ratio between the initial concentration of radionuclides and the final concentration. It is worth mentioning that the treatment of nuclear wastes is preceded by a pre-treatment step that is designed to improve the safety of the management system, and lower radiation exposure and cost of subsequent management elements. The pre-treatment step utilizes waste segregation, component separation and recovery.

Table 1.9 and Table 1.10 list different waste categories and their corresponding technical treatment options (IAEA, 1994b, 1999b; Ojovan and Lee, 2005; Abdel Rahman *et al.*, 2011b). As shown in the tables, these technical options are similar to those applied for conventional industrial wastes. Combined treatment methods are typically used to deal with the variety of chemical compositions of different waste streams. Examples for the utilization of combined methods are given below. A full description of the technical options for treating nuclear wastes will be presented in Chapter 6.

1.4.2.1 Treatment of Front-End NFC Wastes

Currently, countries such as Brazil, Russia, Kazakhstan and Canada are concerned by safety aspects of present and past waste arising from mining and milling activities. The main issues cover mine waste rock, mill tailings and mining and milling wastewater (IAEA, 2005b).

Table 1.10 *Technical treatment options for solid nuclear waste*

Treatment	Techniques	Feature
Mechanical	Low force compaction	Relatively low cost Easy to operate Relatively low volume reduction (2 : 1)
	High force compaction	High volume reduction factor (10 : 1) Good quality wasteform High capital and running cost
	Shredding	Usually performed during pre-treatment
	Dismantling	Applies to large decontaminated metals
	Cutting	Not economical for small waste streams
Thermal	Excess air incineration	High volume reduction factor
	Controlled air incineration	Variable techniques of varying complexity
	Plasma pyrolysis	Volume reduction ratio 95 : 1
	Fluidized bed incineration	
	Plasma arc incineration	Only suitable for advanced nuclear programmes
Chemical decomposition	Acid digestion	Avoids the necessity of high temperature incineration
	Acid stripping	Suitable for biological waste
	Chemical oxidation	No volume reduction
	Photolysis	
	Electrolysis	
	Biochemical	

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The Key Lake mine in Canada is the largest high-grade uranium milling operation in the world, with a licensed annual production capacity of 7.2 million kg of uranium or 18.7 million lb of U_3O_8. Effluent discharged from this site is composed of effluent from the dewatering system installed around the open-pit mines and water returned from the tailings facilities. The treatment method applied to these effluents is bulk neutralization. The Ingulskaya and Smolino mines in Ukraine use a standard system to treat the effluents as illustrated in Figure 1.9 (IAEA, 2004). This system is targeted to reduce the total dissolved solids by using a coagulation/settling process and filtration. The effluent resulting from leaching operations in Zhejiang province in southeast China is treated by mixing with pit water and then directed to an effluent treatment plant that relies on utilization of the ion-exchange technique. The flow process is illustrated in Figure 1.10 (IAEA, 2004).

In Australia, neutralization is used to treat acidic slurries/liquors effluents with lime. The conventional neutralization process was found to produce a large sludge volume with significant moisture content, which promotes seepage and limits the quantity of water available for recycling. This method concentrates heavy metals, radionuclides and dissolved salts in a way that does not comply with the regulatory requirements. Another significant problem is the impact of residual sulphate on aquatic ecosystems and the quality of drinking water resources. A high density sludge method was proposed to improve the sludge characteristics by recycling a substantial proportion of the thickener underflow sludge, which is blended with lime slurry prior to entering the main reaction

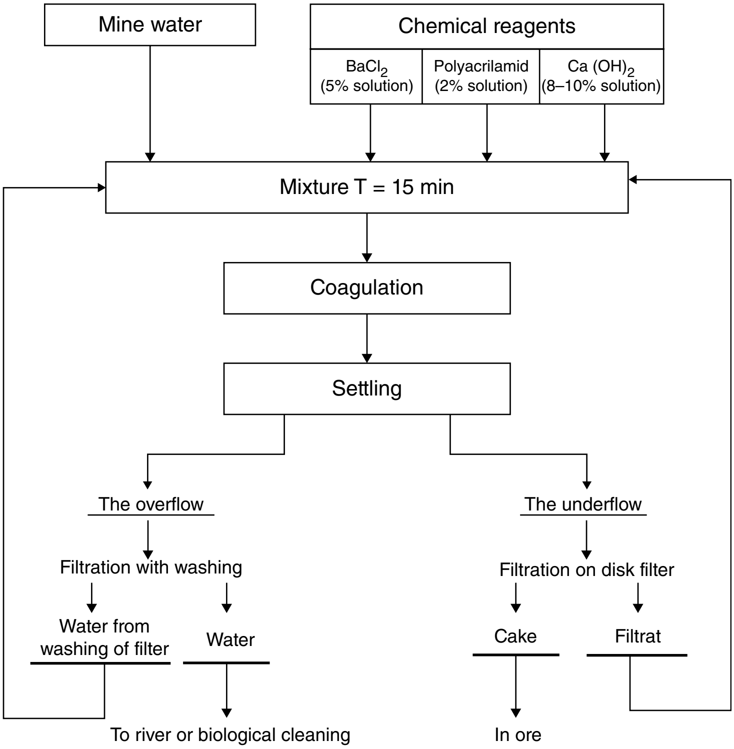

Figure 1.9 *Technological scheme of mine water treatment in Ukraine. Reproduced with permission from IAEA, 2004. © 2004, IAEA*

vessel. The pre-mix ensure the achievement of a dense particulate material compared with the fluffy precipitate normally obtained (IAEA, 2004).

1.4.2.2 Treatment of Nuclear Reactor Operational Wastes

Organic liquid wastes generated during the operation of nuclear reactors may include spent extraction solvents, oils and scintillation liquids. The most commonly used extraction solvent is tributyl phosphate which is usually diluted with a light saturated hydrocarbon. Scintillation liquids consist of non-polar organic solvents such as toluene, xylene and hexane but they may also include biological compounds such as steroids and lipids. The treatment of these organic liquids typically consists of distillation followed by a suitable volume reduction technique, as illustrated in Figure 1.11. Distillation is used as a treatment technique to divide the organic liquid stream into two portions: the first is the recovered organic liquid that can be recycled and used as a fuel for incinerator; and the second is a small volume of organic residues contaminated by radioactive content (IAEA, 2001a).

Liquid aqueous wastes streams generated during the operation of nuclear power plants are treated using combined techniques such as evaporation, precipitation, ion exchange, ultrafiltration and reverse osmosis. For example, the aqueous waste treatment facility at Bruce A nuclear power plant in Ontario, Canada was designed to treat wastes arising from reactors

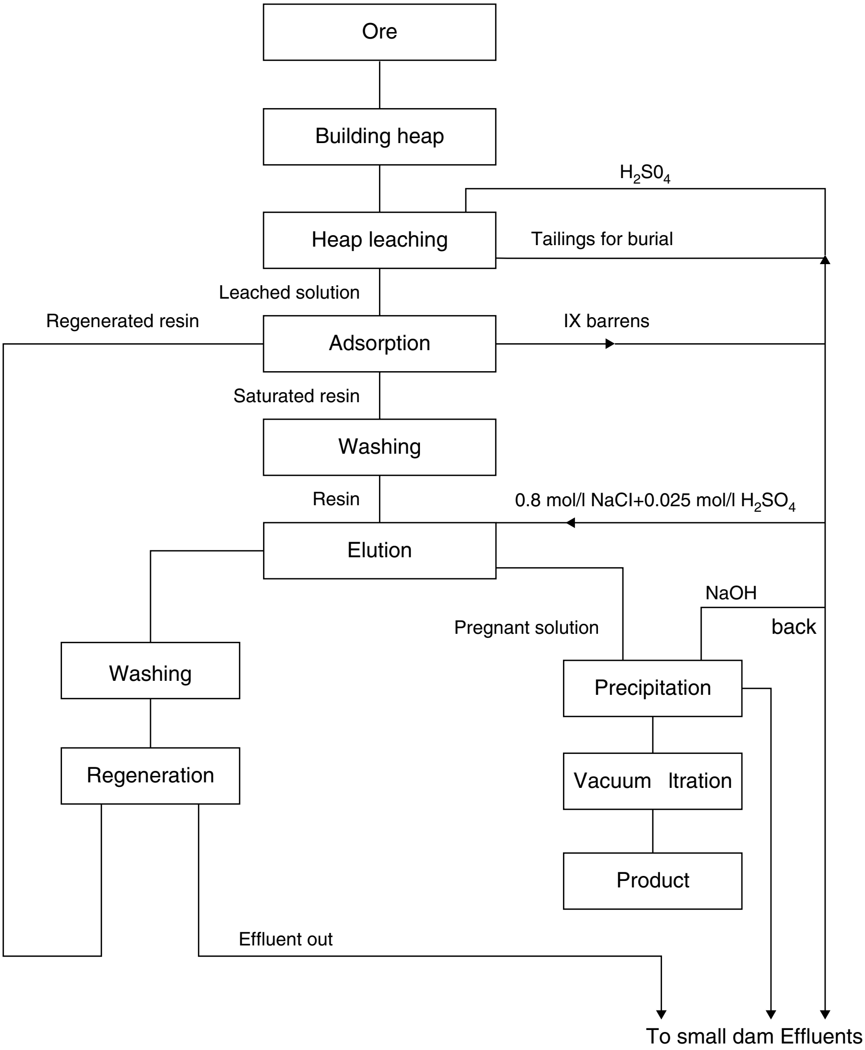

Figure 1.10 *Flow process of the effluent treatment plant in the Zhejiang uranium mine. Reproduced with permission from IAEA, 2004. © 2004, IAEA*

sumps, plastic suite laundry units, central maintenance facilities and volume reduction facilities. As illustrated in Figure 1.12, the system is composed of two subsystems: the first utilizes filtration and ion exchange; and the second is composed of filtration, reverse osmosis and evaporation (IAEA, 2002b).

1.4.2.3 Treatment of Nuclear Centre Wastes

The treatment of aqueous low level radioactive wastes generated during the operation of nuclear research reactors, radioisotope production and research laboratories are also performed using combined treatment techniques. The treatment of low-level aqueous wastes

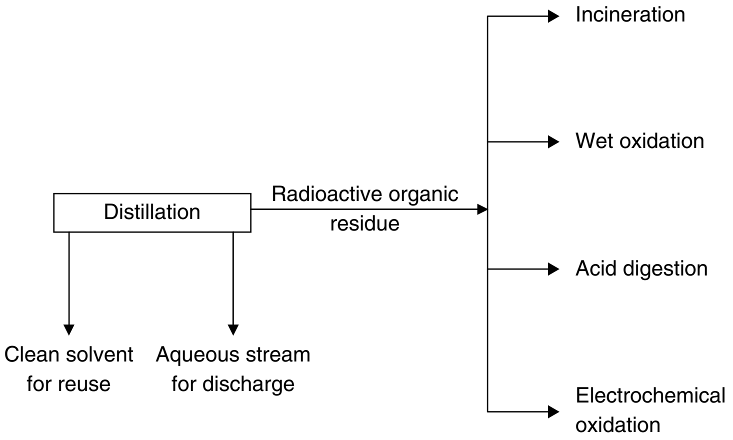

Figure 1.11 *Technological options for treating solvents and scintillation liquids.*

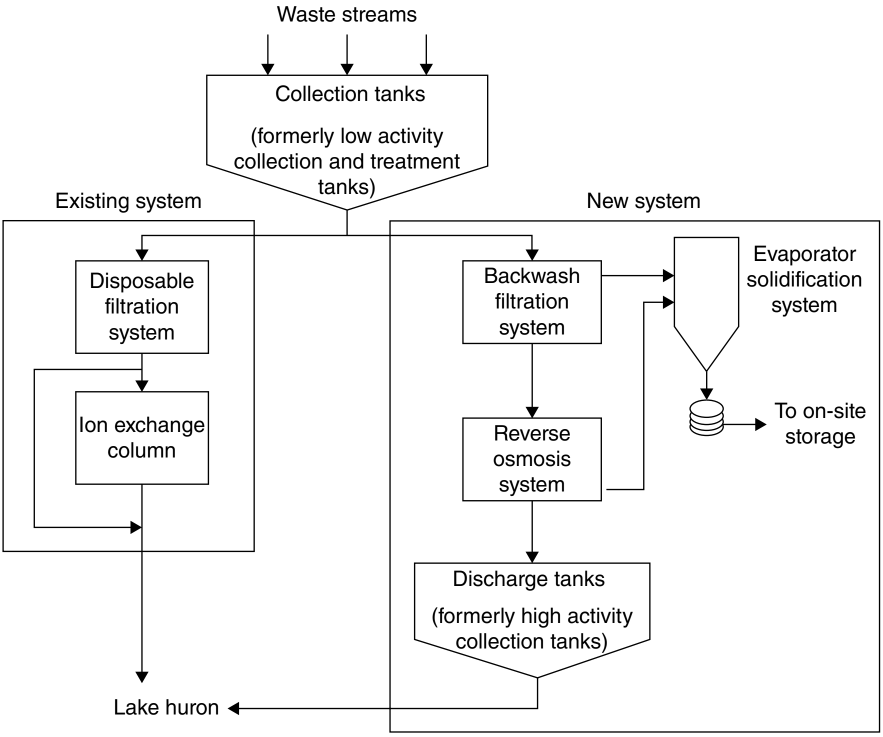

Figure 1.12 *Aqueous liquid waste system at Bruce A nuclear power plant in Ontario, Canada. Reproduced with permission from IAEA, 2002b. © 2002, IAEA*

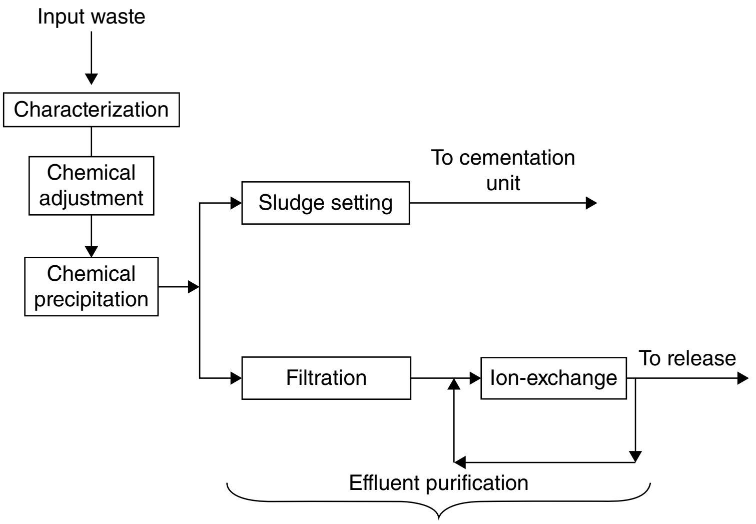

Figure 1.13 *Flow process of the Egyptian low-level radioactive aqueous waste treatment facility. Reproduced with permission from Abdel Rahman, 2009. © 2009, John Wiley & Sons, Ltd*

generated at the nuclear research centres in Egypt is illustrated in Figure 1.13 (Abdel Rahman, 2009). The system consists of precipitation, filtration and ion exchange.

The generated gaseous wastes from the radioisotope production facilities are generally treated using filters. In Canada, the on-site treatment of ^{99}Mo waste is composed of an in-cell off-gas treatment system. These wastes are generated from the dissolver and are scrubbed with nitric acid and distilled water. The gas is then collected into a decay system where noble gases are trapped for a certain period of time prior to release to the cell ventilation system. Radioactive krypton and xenon are trapped in a series of decay columns to allow radioactive krypton and xenon to decay. The cell ventilation system, which consists of a series of high-efficiency particulate air (HEPA) and charcoal filters, is designed to retain particulate material and isotopes of iodine, and thus minimize the release of radioactivity to the environment (IAEA, 1998).

1.4.2.4 Immobilization and Disposal Options

By definition immobilization is the conversion of waste into a wasteform by solidification, embedding or encapsulation which aims to reduce the potential for migration or dispersion of radionuclides during handling, transport, storage and/or disposal (IAEA, 2003a, b). Immobilization includes operations done to enhance the chemical and mechanical properties of the waste. It is performed as a part of the conditioning activities; it aims to provide confinement for the main pollutants in the wasteform. There are different immobilization media that could be used such as cement, cement-based materials, bitumen, glass, ceramics and metals (Ojovan and Lee, 2005; Abdel Rahman *et al.*, 2007). Section 1.5, will discuss their features.

Disposal by definition is the emplacement of waste in an appropriate facility without the intention of retrieval (IAEA, 2003a, b) and is intended to insulate nuclear wastes from the accessible environment. A disposal facility is a permanent end point for radioactive waste that protects people and the environment now and in the future. Disposal options are typically categorized as near surface and deep geological. Near surface disposal facilities include shallow land facilities consisting of disposal units located at or below the ground surface (in the form of trenches, vaults, pits, etc.) and rock cavities or abandoned shallow mines. Geological disposal refers to disposal at greater depths, typically several hundreds of metres below ground. The choice of the disposal option is dependent on the waste type, local conditions, regulatory requirements, national policy principles and consideration of sociopolitical acceptance. Chapter 9 will present waste disposal facilities' design, modelling and different assessment approaches.

1.4.3 Technical Factors that Affect Technology Selection

Technology selection is the core of the waste management system as it affects the characteristics of the waste product within the system and the overall efficiency of the system. The selection of the technological option is bound by many non-technical and technical factors. The non-technical factors include, but are not limited to, cost and fund availability, geographical conditions and physical infrastructure. The technical factors are summarized as follows (IAEA, 2001a):

1. Waste composition is considered the most important technical factor that will affect technology selection. Indeed failure to obtain a clear identification of the waste characteristics can increase the risk of selecting an inappropriate process that produces bad management practices.
2. Exact assessment of generated waste quantity and the generation rate helps in the optimization of the scale of technology application. For example, if the waste generation rate and generated waste quantities are large, this will put constraints on the size of the facility and consequently the justification of the selection of volume reduction technology, human resources and the management costs.
3. The maturity of the technology is a key factor that justifies the selection of specific options. The level of demonstration, types of the waste processed, licensing status, availability of suppliers and services, practical operating experience and information on the current uses of the technologies are elements that help in testing the maturity of the technology.
4. Technology robustness is in terms of capability of being operated under varying operational and maintenance conditions that include sensitivity of the technology to variation of the input waste, operating parameters, complexity of start-up, maintenance, shutdown and decommissioning operations.
5. The flexibility of the technology to process different waste streams addresses a balance between a small simple specific technology which the generator of a single waste stream might use and a larger, more versatile technology that might be used at a central processing facility.
6. The site characteristics have implications for both waste processing and storage facilities. The characteristics include hydrogeology, seismicity, climate, the proximity of airports, populated areas, water, power and personnel.

1.5 Wasteform Materials

To ensure the confinement of nuclear wastes, the treated wastes are immobilized using suitable immobilization media. The immobilization of nuclear wastes could be achieved by solidification, embedding and/or encapsulation. A number of immobilization media have been used including cement, bitumen, polymer, ceramics and metals (Lee *et al.*, 2013).

Cementation is the most widely used technique for the immobilization of low- and intermediate-level radioactive wastes. It relies on using cement as primary binder to immobilize radioactive contaminants. The worldwide utilization of this technique is supported by the good mechanical characteristics of cement and its radiation and thermal stability. The industrial application of cementation proved as simple and did not require high capital and operating costs. Cementitious wasteform contains in addition to cement and waste, water and additives. Additives are used to improve either the mechanical performance of the final waste matrix and/or the retention of radionuclides in the wasteform (Ojovan and Lee, 2005, 2014; Abdel Rahman, 2012). Different additive types and their properties are discussed in Section 6.5. During immobilization two simultaneous processes occur, namely stabilization and solidification. The wastes are stabilized by converting the radionuclides to a less mobile form as a result of chemical changes, whereas solidifying these wastes improves their mechanical performance (Batchelor, 2006; Abdel Rahman and Zaki, 2009). Different cementation technologies will be presented in detail in Chapter 7.

Bitumen is a viscous hydrocarbon used to solidify and stabilize radioactive materials. Bitumen immobilizes waste mainly by encapsulation. The advantages of bitumen as a wasteform are its simplicity of production, low operating cost and leach resistant characteristics. Bitumen is applicable to very low heat generation waste (typically <40 TBq/m^3) that results from the treatment of low- and intermediate-level liquid effluents (Abdel Rahman, 2012). Bitumen is suitable to host water-soluble wastes such as bottom residues from evaporation treatment and spent organic ion exchangers (IAEA, 2001a). With this technique, nuclear wastes are embedded in hot bitumen and physically encapsulated when the bitumen cools. The operating procedure showed that bituminization is a complex and more expensive process compared with cementation. Despite the achieved volume reduction and its compatibility with different waste streams, the produced wasteform has a relatively low mechanical performance and low fire resistance. The bituminized product has a very low permeability and solubility in water and is compatible with most environmental conditions. This kind of immobilization media is used with restrictions for wastes that contain strongly oxidizing components such as nitrates. Special care should be taken with this wasteform during storage owing to its flammability. Bitumen was used to solidify evaporation concentration, spent ion exchange and filter cartridge (IAEA, 1993; Guzella and Da Silva, 2001; Ojovan and Lee, 2014). A typical flow diagram of the bituminization process is shown in Figure 1.14.

Different polymers have been used as immobilizing media, the operation of this technique is relatively expensive and the process is complex. The main advantages of choosing this technique are the high waste loading and good retention of contaminants.

Vitrification is one of the most important immobilization techniques due to the characteristics of vitrified wastes such as their small volume, and high durability and stability in corrosive environments (IAEA, 2001a). This process is typically applied to high-level nuclear wastes. Vitrification is conducted using high processing temperatures ranging from

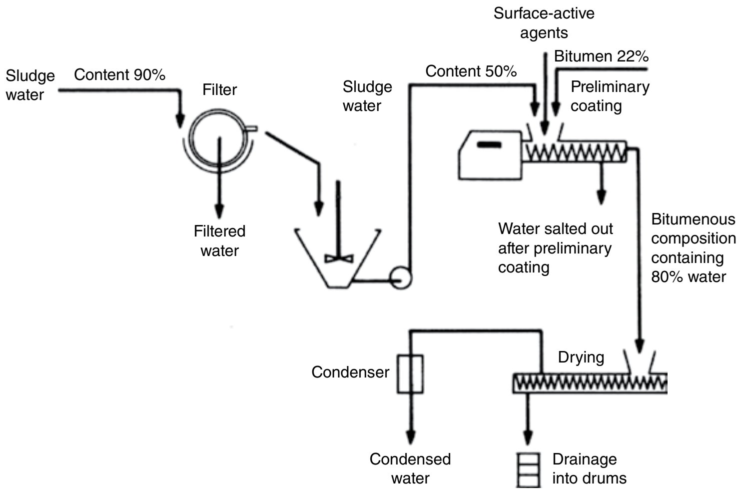

Figure 1.14 Schematic of the extruder type bituminization processes at Marcoule, France. Reproduced with permission from Ojovan and Lee, 2014. © 2014, Elsevier

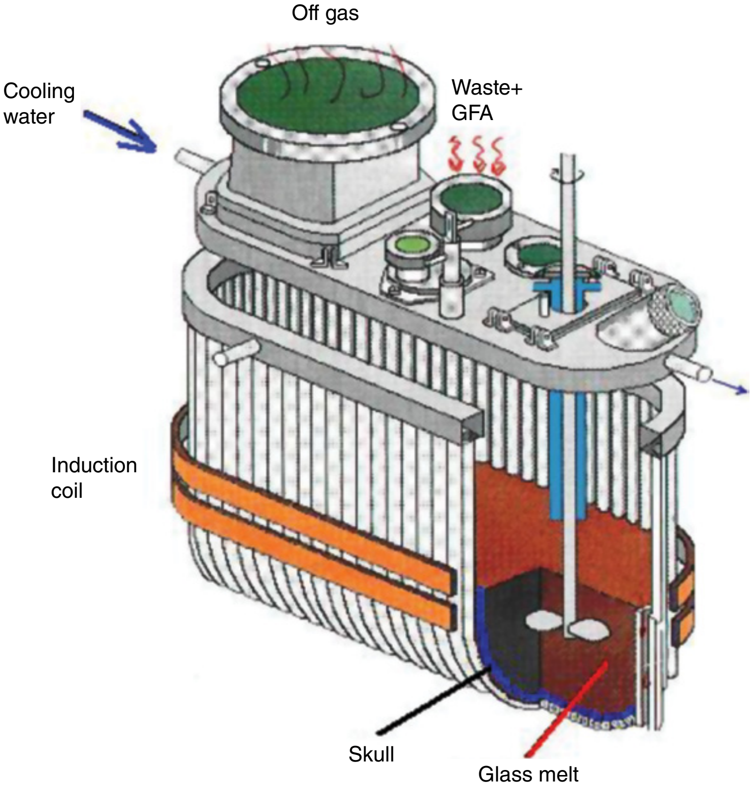

Figure 1.15 Cold crucible melter at FSUE RADON, Russia. GFA, glass-forming additives. Reproduced from Ojovan and Lee, 2014. © 2014, Elsevier

950 to 1250 °C. The highest degree of volume reduction and safety is achieved through vitrification although this is the most complex and expensive method requiring a relatively high initial capital investment. The composition of the produced wasteform is typically complex since it contains fission products, transuranic, corrosion products and oxides. The most commonly used vitrification media are borosilicate and phosphate glasses (Ojovan and Lee, 2011). Cold crucible melters are used to immobilize nuclear wastes where the waste and the glass forming additives are introduced to the melter. Figure 1.15 illustrates the vitrification melter used at FSUE RADON in Russia (Lifanov *et al.*, 2003).

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2

Cements: Portland Cement

2.1 Cements

Cements are powdery mineral binders, which after mixing with water or water solutions of some salts form a yielding mass able to go hard over time and convert into a stone-like state as a result of physico-chemical processes. The development history of types, production and use of cementitious materials is closely associated with the history of civilization. One of the first cementitious materials, which was used by humans tens of thousands years ago, was unburnt clay. Over time, more than 5.5–6 thousand years ago, methods were discovered for producing gypsum and lime by burning the appropriate rocks, which differed in increased strength in comparison with cementing materials from unburnt clay, but at the same time they had low water resistance.

Gypsum and lime cements were the only types of cements used by humans for several millennia. Different ways of increasing their strength and water resistance were sought by introducing various additives up to the end of the eighteenth and into the middle of the nineteenth centuries, whereupon the English invented the methods of producing cements of enhanced and high water resistance. In 1756 J. Smith produced the first water-resistant lime-based binder by burning a limestone with clay content up to 20%, termed hydraulic lime, and in 1796 J. Parker produced the second water-resistant cement of increased strength by burning limestone with more than 25% clay content, termed Roman cement.

A breakthrough in the history of civilization was the invention of high-strength and water-resistant clinker cement, known as Portland cement, in 1824 by J. Aspdin. The world production and use of Portland cement, starting from the middle of the nineteenth century, constantly

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Cementitious Materials for Nuclear Waste Immobilization, First Edition. Rehab O. Abdel Rahman,
Ravil Z. Rakhimov, Nailia R. Rakhimova and Michael I. Ojovan.

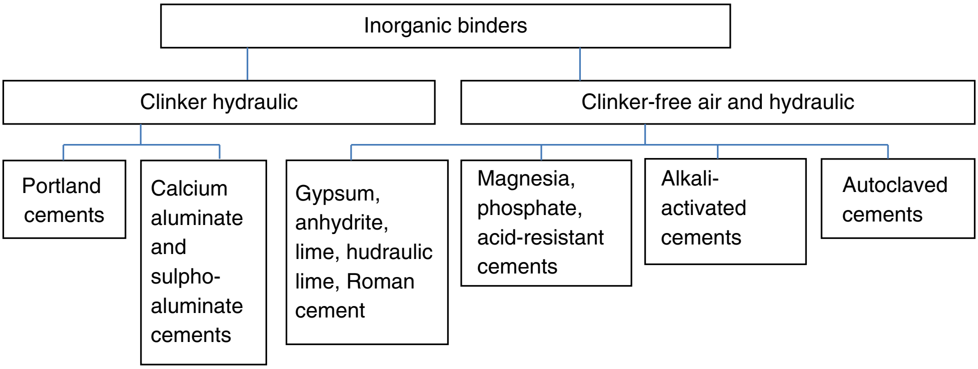

Figure 2.1 *Extended classification of mineral binders*

grew and has now reached more than 2.5 billion t per year. At the same time the variety of cementitious materials continuously widened; the classification of mineral binders is shown in Figure 2.1.

Having gained widespread use in the twentieth century, introduction of mineral and chemical additives increased the development from several to hundreds of types of each of the cements shown in Figure 2.1. In the meantime, the bulk of cementitious materials being produced and used nowadays represents ordinary Portland cement (OPC)(OPC in Great Britain, CEM I in other countries in the EU and CIS and ‘type I Portland cement’ in the USA).

2.2 Portland Cement: Manufacture, Mineral Composition, Properties

Portland cement is a hydraulic binder with a composition dominated by calcium silicates (70–80%) and which is a milled product of clinker with the addition of 3–5% gypsum. A clinker represents a granular material with the size dependent on the type of kiln used with sizes up to 10–20 mm, or up to 50–60 mm, achieved by burning the raw mixture from limestone and clay in the ratio 3:1 till clinkerization occurs at 1450°C. The chemical composition of the raw mixture must produce Portland cement clinker with the oxide-based chemical composition (in wt%): CaO, 63–66; SiO_2, 21–24; Al_2O_3, 4–8; Fe_2O_3, 2–4; MgO, 0.5–5; SO_3, 0.3–1; $Na_2O + K_2O$, 0.4–1; $TiO_2 + Cr_2O_3$, 0.2–0.5.

The manufacture of Portland cement includes the following operations: extraction (mining) of raw mixture and its delivery to the factory, burning of raw mixture until clinkerization (clinker formation, clinker grinding with addition of gypsum), Portland cement formation, storage and packaging.

The methods of preparing raw mixturesaccordingly determine the methods of manufacturing Portland cement – wet, combined and dry (Figure 2.2).

When burning raw mixtures as a result of a number of chemical reactions, a complex of minerals is formed, composing the clinker, which can be separated into compositions of different forms, sizes and structures.

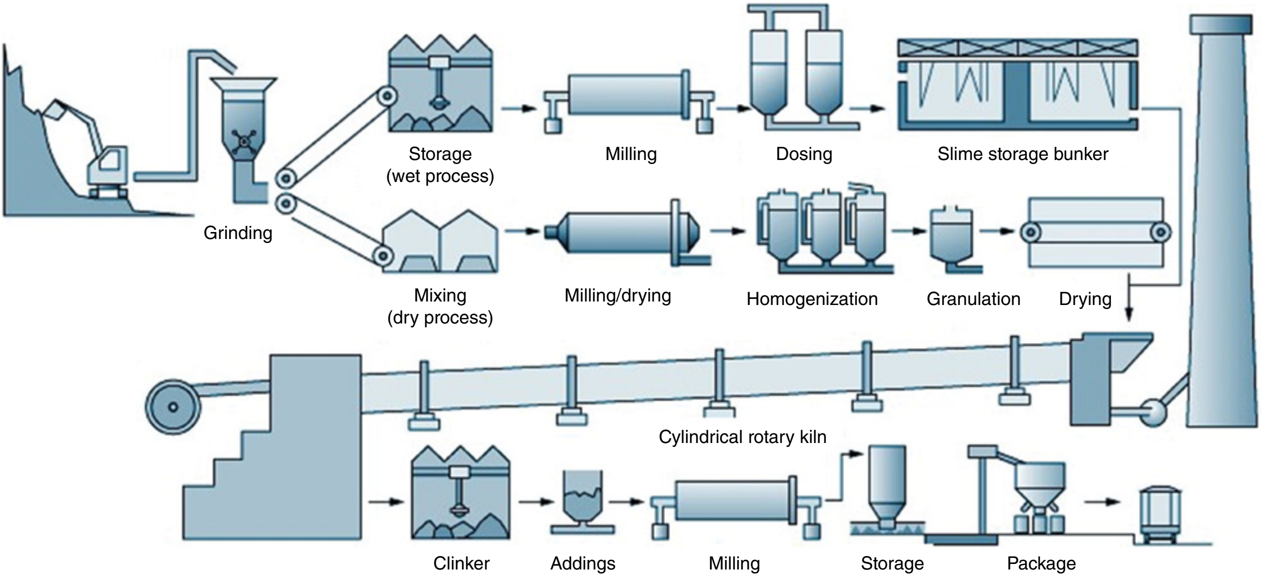

Figure 2.2 *Production technology of Portland cement*

2.3 Phase and Mineral Composition of Ordinary Portland Cement

The phase and mineral composition of OPC are determined by the mineral composition of cement clinker and additives of gypsum.

Portland cement clinker crystallized to different degrees and containing a glassy phase (5–15%) contains the following minerals:

- tricalcium silicate – 3 $CaO{\cdot}SiO_2$ (C_3S);
- dicalcium silicate – 2 $CaO{\cdot}SiO_2$(C_2S);
- tricalcium aluminate – 3 $CaO{\cdot}Al_2O_3$ (C_3A);
- tetracalcium aluminoferrite – 4 $CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$ (C_4AF).

In addition the clinker contains:

- CaO free – up to 1%;
- MgO free and as a part of other phases – 1–5%;
- Na_2O and K_2O in alkali-containing phases – up to 1%.

The above mentioned minerals in Portland cement do not consist of pure phases but represent solid solutions, containing different types and numbers of oxide impurities: aluminium, iron, chromium, magnesium, manganese, phosphorus, potassium and so on. Though the content of these oxides is not very high, they influence the structure and properties of the cement paste both during hardening and under operational conditions.

The properties of Portland cement depend on:

- content and ratio of clinker minerals;
- dispersity and particle size distribution of cement;
- type and content of mineral and chemical admixtures.

Table 2.1 presents the Portland cement clinker classification on the basis of mineral composition (Dvorkin and Dvorkin, 2011).

The C_3S content for normal clinkers is 52–60 wt% at current levels of cement production technology.

Modern cement plants produce the following cements: normal (C_3S = 40–60%, C_2S = 15–40%), high alite (C_3S > 60%), high-aluminate (C_3A > 9%), medium-aluminate (C_3A = 6–9%) and low-aluminate (C_3A < 6%).

Table 2.1 *Portland cement clinker classification depending on mineral composition*

Portland cement clinker	Content of minerals (wt%)			
	C_3S	C_2S	C_3A	C_4AF
Alite	>60	<15	—	—
Normal	60–37.5	15–37.5	—	—
Belite	<37.5	>37.5	—	—
Aluminate	—	—	>15	<10
Normal (in terms of content of C_3A)	—	—	7–15	10–18
Zeolitic	—	—	<7	>18

Table 2.2 ASTM classification of Portland cements

Type/designation according to C150	Special characteristics/ intended use	Composition			
		C_3S	C_2S	C_3A	C_4AF
I	Normal, general purpose	50	24	11	8
II	Moderate sulphate resistance/ moderate heat of hydration	42	33	5	13
III	High early strength	60	13	9	8
IV	Low heat of hydration	26	50	5	12
V	High sulphate resistance	40	40	4	9

Currently the most popular cements are five types of Portland cement, described in the ASTM C-150 standard, the mineral composition and the distinctive names of which are shown in Table 2.2.

The content of the minerals in cements is established in Russia based on the properties of different types of Portland cement:

- sulphate-resistant ($C_3S \le 50\%$, $C_3A \le 5\%$);
- cements with moderate heat of hydration ($C_3S \le 50\%$, $C_3A \le 8\%$);
- rapid hardening ($C_3S + C_3A = 60–65\%$);
- super rapid hardening ($C_3S = 65–6\%$, $C_3A \le 8\%$);
- extra rapid hardening ($C_3S = 65–68\%$, $C_3A \le 8\%$ + additives CaF_2 and $CaCl_2$ when performing clinker grinding).

Rapid-, super rapid- and extra rapid hardening Portland cements are characterized by fineness of grinding of about 400 m^2/kg.

2.4 Properties of Portland Cement

Property values of Portland cements fluctuate over a wide range depending on their composition and fineness of grinding.

The properties of OPC are characterized by the following values:

- specific gravity 3.1–3.2 g/cm^3;
- bulk density:
    - in friable state 0.9–1.1 g/cm^3;
    - in compacted state 1.3–1.7 g/cm^3;
- fineness of grinding 250–350 m^2/kg;
- normal consistency 24–28%;
- setting time:
    - initial – not sooner than 45 min;
    - final – not later than 10 h;
- soundness – absence of radial cracks till the cement pastille edges and surface bents are larger than 2 mm;
- strength class 32.5 N(R)–52.5 N(R).

Two classes of early strength are included for each class of standard strength: a class with ordinary early strength, indicated by N; and a class with high early strength, indicated by R [see table 2 of EN 197-1:2000 (2000), p. 15].

The property values of Portland cement materials depend on the specifics of hardening, which are determined by their interaction with water. An interacting process of cementitious materials with water is termed hydration.

2.5 Hydration of Portland Cement

Solution of the tasks for the efficiency of radioactive waste immobilization in cement matrixes is impossible without the knowledge of the hydration mechanism and structure formation of its products. The term 'hydration' in cement chemistry means all the changes which occur when anhydrous cement or one of the constituents of its phases is mixed with water (Baykov, 1923).

By now the results of the numerous experimental and theoretical studies of the processes of hydration and hardening of the binders are well-known, having been performed from the end of the nineteenth century to until very recently (Le Chatelies, 1919; Baykov, 1923; Lea, 1956; Rebinder, 1956; Ramachadran *et al.*, 1981; Polak *et al.*, 1990; Taylor, 1997; Scrivener and Nonat, 2011; Plugin *et al.*, 2012; Scherer *et al.*, 2012).

Depending on the existing experimental and theoretical data, the theories of hardening developed from simple to complicated. In addition hardening processes were considered at first at the rough macroscopic level. In recent decades hardening processes have been studied at the molecular, ionic and electronic levels (Stark, 2011), and simulation computer modelling and other kinds of modelling are being developed. Nowadays atomic-level modelling plays a key role in the development of the science of cement materials (Pelleng and Kushima, 2009; Stark, 2011). A unified theory of hardening of the cementitious materials has not been created yet (Scrivener and Nonat, 2011; Plugin *et al.*, 2012). However, there are many facts and general provisions regarding the mechanism of their hydration and hardening, which are recognized by the majority of researchers as indisputable and these are listed in the following.

A base for interpretation of the complex processes taking place on hydration of the cements under different conditions is understanding the hydration of Portland cement clinker constituents.

2.5.1 Hydration and Hydraulic Activity of Clinker Phases and Portland Cement

The hydration activity of mineral binders is their ability to interact with water, for example the ability to form low solubility products with a structure which provides high strength and other properties as a result of physical and mechanical processes when interacting with water.

The hydration activity of mineral binders is revealed both with and without their chemical interaction with water, and is always accompanied by thermal processes. It can be therefore characterized by the degree of hydration or the amount of heat evolved. Interaction of cementitious materials with water is accompanied by heat evolution, the regularity and amount of which describe the process and degree of their hydration (Copeland *et al.*, 1960; Taylor, 1997). In this connection the total heat effect Q is given by:

$$Q = Q_i + Q_{ch} + Q_{cr} + Q_W + Q_s - Q_d, \qquad (2.1)$$

where Q_i is the heat due to water adsorption on the initial binder, Q_{ch} is the heat of chemical reaction, Q_{cr} is the heat of reaction product crystallization, Q_W is the heat due to water adsorption by the new growth products, Q_s is the heat of solvation and Q_d is the heat of dissolution.

Hydration and hydraulic activity of Portland cement is determined by the respective activities of its clinker phases, clinker phase content, size and defect structure of their crystals, size of the clinker particles, specific surface area and granulometric composition of cement, water/cement (w/c) ratio, hardening temperature and so on.

Figure 2.3 shows the hydration activity of forming phases of a Portland cement clinker (Taylor, 1997; Stark, 2000).

The fact that phases forming the clinker are hydraulically active is a necessary but not sufficient condition to form a cement stone. As a result of the physico-chemical processes at hydration, the products formed have different compositions, structure and properties. Figure 2.4 shows the compressive strength of products formed on hydration of Portland cement clinker constituent phases as a function of hydration time.

Aluminate and aluminoferrite phases react with water fast but the hydration products of these phases do not have high strength. In contrast, the hydration products of alite and belite, have high strength and they are essential in forming the hydraulic activity of Portland cement.

Studies often give data on the degree of hydration and strength of hardened paste and the constituents differing in the level achieved at the same period of hardening, as shown in

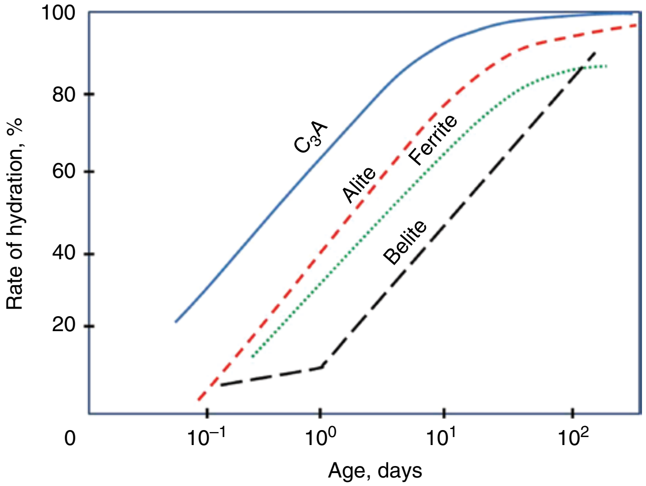

Figure 2.3 *Hydration activity of the constituents forming Portland cement phases depending on hardening duration*

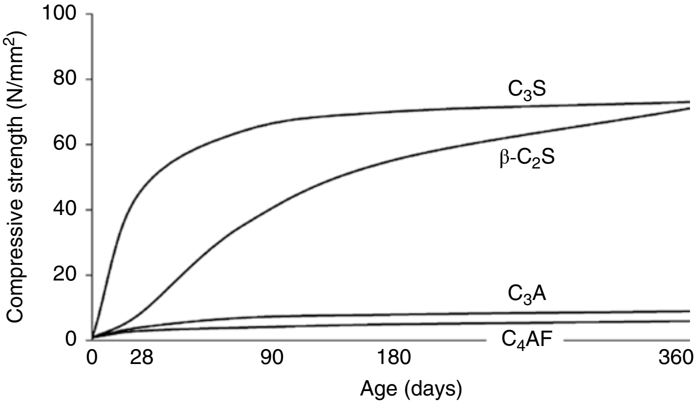

Figure 2.4 Compressive strength of hydration products of Portland cement clinker constituent phases

Figure 2.3 and Figure 2.4. This is explained by the difference of the constituents being analysed having different specific surface areas, grain size composition, w/c ratios, and presence and content of impurities. However, generic relations of hydration and hydraulic activity of these constituents correspond to those presented in Figure 2.3 and Figure 2.4.

The research results on hydration and hydraulic activity of individual clinker minerals can be used when calculating the properties of Portland cement.

For example, the amount of heat, ΔH^t, emitted as a result of hydration of a cement of given composition to a certain period of time t can be calculated using the additivity concept (Copeland *et al.*, 1960) according to the formula:

$$\Delta H^t = a\cdot(\mathrm{C_3S}) + b\cdot(\mathrm{C_2S}) + c\cdot(\mathrm{C_3A}) + d\cdot(\mathrm{C_4AF}), \tag{2.2}$$

where the mass fractions of interacting phases are shown in parentheses. The coefficients a, b, c and d are given in Table 2.3 for w/c ratio 0.4, hydration temperature 21°C and at different times of the hydration process (ages).

Figure 2.5 gives the average integral curves of heat evolution, calculated using Eq. (2.1) which show differences in hydration activity of several Portland cements with different mineral compositions within a period of hardening from 3 days up to 13 years.

The hydraulic activity R^t at time t of a Portland cement stone characterized by its content of the main active minerals, forming phases of Portland cement clinker, certain w/c ratio used, hardening temperature T, and air humidity W can be approximately calculated using the additivity concept according to the formula:

$$R^t = n\cdot R^t(\mathrm{C_3S}) + m\cdot R^t(\mathrm{C_2S}) + p\cdot R^t(\mathrm{C_3A}) + r\cdot R^t(\mathrm{C_4AF}), \tag{2.3}$$

where $R^t(\mathrm{C_3S})$, $R^t(\mathrm{C_2S})$, $R^t(\mathrm{C_3A})$, $R^t(\mathrm{C_4AF})$ are the strengths of hardened monomeric mineral cement pastes with the same w/c at temperature T and air humidity W, and n, m, p and r are the weight fractions of monomeric phases, for example $\mathrm{C_3S}$, $\mathrm{C_2S}$, $\mathrm{C_3A}$ and $\mathrm{C_4AF}$.

Table 2.3 *The coefficients needed for the calculation of the cumulative heat of cement paste using Eq. (2.1) at w/c = 0.4 and temperature 21°C (Collepardi et al., 1972)*

Mineral	Coefficient	Coefficient (kJ/kg) at given age							Enthalpy of hydration (kJ/mol)
		3 days	7 days	28 days	90 days	1 year	6.5 years	13 years	
C_3S	*a*	243	222	126	435	490	490	510	−517 ± 13
β-C_2S	*b*	50	42	105	176	226	222	247	−262
C_3A	*c*	887	1556	1377	1301	1167	1372	1356	−1144
C_4AF	*d*	289	494	494	410	377	464	427	−418

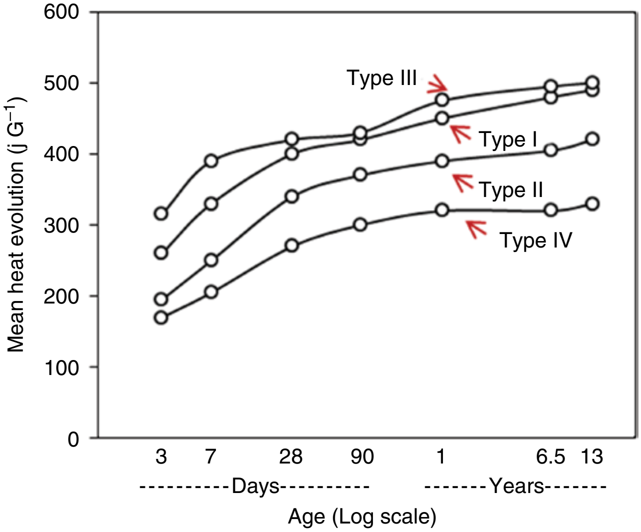

Figure 2.5 *Average cumulative heat evolution for a total of 20 Portland cements of USA types I, II, III and IV, hydrated at w/c = 0.4 and 21°C*

2.5.2 Process Chemistry, Products and Hydration Stages

Portland cement is a complex system, consisting of a mixture of solid solutions of the minerals C_3S, C_2S, C_3A, C_4AF, containing different types and amounts of impurity oxides.

In order to have some idea about the interaction of Portland cement of such complex composition with water, it is appropriate first to study the reactions of individual clinker components with water, and then of complex processes, connected with the appearance of new formations in a mixture of cement and water (Bogue, 1947; Stein and Stevels, 1964; Collepardi *et al.*, 1972; Volgensky, 1986; Mchedlov-Petrosyan, 1988; Kuznetsova *et al.*, 1989).

Tricalcium and dicalcium silicate content ranges from 75 to 80% of the mass of cement. In general terms the reactions of interaction of C_3S and C_2S with water can be presented as (Ramachadran *et al.*, 1981; Stark, 2000):

$$C_3S+(y+z)H \rightarrow C_xSH_y + zCH,$$

for example:

$$2(3CaO\cdot SiO_2)+6H_2O=3CaO\cdot 2SiO_2\cdot 3H_2O+3Ca(OH)_2 \tag{2.4}$$

and

$$C_2S+(2-x+y)H \rightarrow C_xSH_y + (2-x)CH$$

for example:

$$2(2CaO\cdot SiO_2)+4H_2O=3CaO\cdot 2SiO_2\cdot 3H_2O+Ca(OH)_2 \tag{2.5}$$

When hydration of alite and belite occurs, calcium silicate hydrates are formed with a composition and degree of crystallinity which change over wide ranges.

Certain ideas about the processes of hydration of Portland cement and its components have been developed, particularly of its main phase – hydration of C_3S (Ramachadran *et al.*, 1981; Taylor, 1997; Scrivener and Nonat, 2011). The kinetic curve of hydration of C_3S is divided into five stages (Figure 2.6): stage 1, pre-induction with decreasing dissolution; stage 2, induction period, stage 3, acceleration period; stage 4, deceleration period; and stage 5, slowly on-going hydration.

Calcium silicate hydrates are formed as a result of alite interaction with water, which have compositions dependent on the ambient temperature and concentration of calcium hydroxide in the liquid phase. Interaction with water and yield of ions into solution with formation of primary hydrates start immediately after the contact of alite particles with water.

In the first stage a jump of heat evolution rate is observed. Splitting of –Ca–O–Ca– bonds occurs in the near-surface zones of alite:

$$-SiO-Ca-O-Ca-OSi+H_2O=Si-Ca-OH+OH^- + -SiO-Ca^+ \tag{2.6}$$

The reaction takes place as a result of water sorption by C_3S grains and it is also accompanied by parallel dissolution of about one molecular layer of grain material. As a result of this reaction in the solution hydroxide ions appear. Bond hydrolysis causes Ca^{2+}, $CaOH^+$ and anions of silicic acid to appear in the solution. Silicate ions from the solution are laid aside near the surface of the alite grains, forming membrane-like shells made of primarily calcium silicate hydrate C_3SH_n, which is then exposed to a fast hydrolysis with formation of the hydration product having a smaller ratio of C/S (secondary and tertiary calcium silicate hydrates). During the second stage the reaction rate is very low,

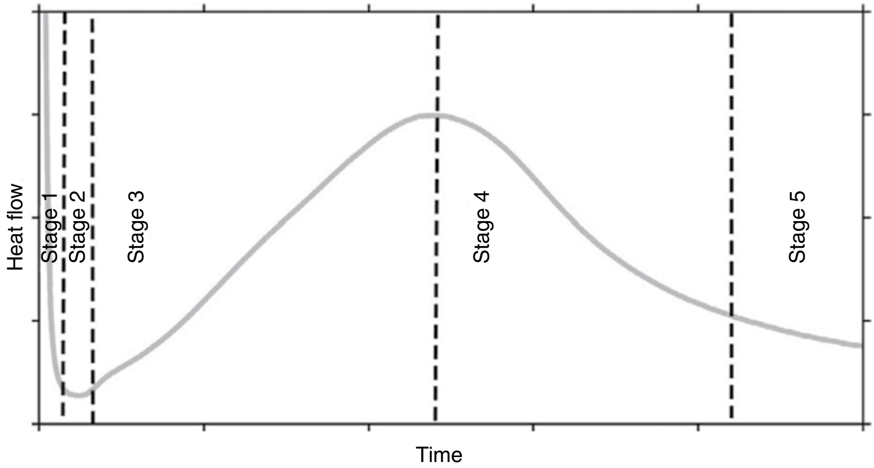

Figure 2.6 *Rate of heat evolution during hydration of alite (w/c = 0.4). Reproduced with permission from Scrivener and Nonat, 2011 © 2011, Elsevier*

however at the same time the dissolution of C_3S continues and the pH of the solution increases to 12.5.

After reaching a certain critical concentration of calcium and hydroxyl ions, fast hydration of C_3S with the formation of $Ca(OH)_2$ and calcium silicate hydrate (third stage) starts.

The mechanism, causing the induction period and its subsequent ending, is explained in different ways (Bogue, 1947; Stein and Stevels, 1964; Collepardi *et al.*, 1972). According to Stein and Stevels (1964) and Gallucci *et al.* (2010) a thin layer of 'nuclei' of calcium silicate hydrate is formed on the surface of C_3S grains. Bullard and Flatt (2010) present a hypothesis of 'stage of slow dissolution', according to which a shell is not formed on the surface of C_3S grains, however the active sites of dissolution are deactivated. In the opinion of Scrivener and Nonat (2011) the induction period can be caused by the influence of changing solution concentration, and in this connection a theory of solution controlled dissolution was advanced.

In the third stage of cement hydration a reaction occurs with a rise in heat evolution with self-acceleration which reaches a maximum rate by the end. The starting time of the third stage is the starting time of cement paste setting which occurs as long as the third stage lasts (Rebinder, 1956).

During the fourth stage of cement hydration the reaction rate of C_3S interaction with water and the heat evolution are gradually decreasing.

In the last fifth stage (20–24 h after the mixing of C_3S with water) the hydration rate is controlled by diffusion-controlled processes which are accompanied by low heat evolution and the formation of a small number of hydration products.

During all five C_3S hydration stages hydration products are formed at different rates; these are calcium silicate hydrates and portlandite, $Ca(OH)_2$. The calcium silicate hydrates, being formed at room and elevated (up to 100°C) temperatures, are characterized by a very low degree of crystallization and denoted by Taylor's (1997) general formula CSH. In accordance with their gel-like structure they are also called gel phase.

All calcium silicate hydrates formed are similar in structure to natural mineral tobermorite, having an average composition $C_5S_6H_5$ and the parameter for the elementary cell is equal to 1.13 nm. However, because the compositions and *a* parameters of calcium silicate hydrates and tobermorite are different, the calcium silicate hydrates are called tobermorite-like minerals. In general they are divided into poorly crystallized tobermorites with $CaO:SiO_2 < 1.5$ for CSH(I) according to Taylor (1997) or CSH(B) according to Bogue (1947) with $CaO:SiO_2 > 1.5$ for CSH(II) and C_2SH_2.

CSH(I) has a $CaO:SiO_2$ ratio in the range of 0.8–1.5, and contains 0.5–2.5 water molecules. It is crystallized in the form of a layered structure made out of thin plates like foils which are frequently twisted. The plates are 2–3 nm thick, 40–55 nm wide and about 1 μm long. The water is placed between the layers of crystallized structures. The specific surface area is 376 m^2/g at two-layer thickness and 252 m^2/g at three-layer thickness.

CSH(II) has a $CaO:SiO_2$ ratio in the range of 1.5–2, and contains 2–4 water molecules. It is crystallized in the form of individual fibres and fibre bunches. It rarely forms wavy-like plates like foils.

The tobermorite gel, CSH(III), has $CaO:SiO_2 \geq 1.5$. During the first stage of the C_3S hydration process a low basic gel is formed, with its basicity growing with increase in degree of hydration. This can be due to change in the structure of colloid particles which compose it, because of adsorption of Ca^{2+} from the solution, or due to intercalation of particles by amorphous $Ca(OH)_2$. The chemical composition and physical structure of the gel can be irregular in its whole mass. The gel forms flocks and aggregates, consisting of rounded particles, thin scales of irregular shape, particles of tubular construction and needles, fibrous formations as big as 0.1–1.0 μm and smaller.

Hydration of C_2S occurs in a similar manner as for C_3S, however at significantly lower rates and with significantly less heat evolved. Its curve of heat evolution does not have such a clear peak as that in Figure 2.6.

C_3A out of all the clinker minerals has the highest reactivity. In the absence of sulphates C_3A immediately reacts with water with the formation of primary products:

$$2(3CaO \cdot Al_2O_3) + 21H_2O \rightarrow 4CaO \cdot Al_2O_3 \cdot 13H_2O + 2CaO \cdot Al_2O_3 \cdot 8H_2O \qquad (2.7)$$

Primary unstable calcium aluminate hydrates have the form of hexagonal plate crystals. These form a fluffy water-permeable shell on the surface of C_3A grains. On further interaction primary unstable calcium aluminate hydrates form a stable product, C_3AH_6:

$$4CaO \cdot Al_2O_3 \cdot 13H_2O + 2CaO \cdot Al_2O_3 \cdot 8H_2O \rightarrow 2(3CaO \cdot Al_2O_3 \cdot 6H_2O) + 9H_2O \qquad (2.8)$$

Cubic-shaped C_3AH_6 crystals also take part in forming fluffy water-permeable shells on the surface of C_3A grains.

Fluffy shells formed practically do not prevent or slow down the process of C_3A hydration, which ends by a quick 'false' setting and hardening of a hydrated C_3A paste. The resulting product however is significantly inferior in strength to calcium silicate hydrates, and impedes the normal calcium silicate hydration process. Gypsum is added into the system in order to facilitate calcium silicate hydration in the presence of C_3A. It slows C_3A hydration due to formation of a dense film made of thin, needle-shaped and prismatic crystals of ettringite on the surface of its grains via the reaction:

$$3CaO \cdot Al_2O_3 + CuSO_4 \cdot 2H_2O + 26H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O \tag{2.9}$$

where the ettringite is a hydrated calcium sulphoaluminate mineral.

Formation of ettringite in the cement paste introduces strong tensions and significant deformations as the volume of the C_3A hydration products is more than 7.5 times larger than that of C_3A.

The *C_4AF hydration reaction* proceeds in a complicated manner with the formation of different primary crystal hydrates dependent on the gypsum content (Pelleng and Kushima, 2009):

$$\begin{aligned} &2\left(4CaO \cdot Al_2O_3 \cdot Fe_2O_3\right) + 32H_2O \rightarrow 4CaO\left(Al_2O_3, Fe_2O_3\right) \cdot 13H_2O \\ &+ 2\left[2CaO\left(Al_2O_3, Fe_2O_3\right) \cdot 8H_2O\right] + \left(Al_2O_3, Fe_2O_3\right) \cdot 3H_2O. \end{aligned} \tag{2.10}$$

$(Al_2O_3,Fe_2O_3)H_2O$ is a gel-like mix of $Al(OH)_3$ and $Fe(OH)_3$. When interacting, unstable primary hydrated aluminoferrites form stable products, $3CaO(Al_2O_3 \cdot Fe_2O_3) \cdot 6H_2O$.

Hydration of C_4AF-gypsum mix is accompanied by the formation of trisulphate $3CaO(Al_2O_3 \cdot Fe_2O_3) \cdot 3CaSO_4 \cdot 32H_2O$ (AF_t) and monosulphate aluminoferrite $3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$ (AF_m) phases and hydroxides, $Al(OH)_3$,$Fe(OH)_3$. Gypsum slows down C_4AF hydration more efficiently than C_3A. However, cements with high C_3A content are not stable under the action of sulphates, whereas cements with high C_4AF content are rather stable. Ettringites are not formed in high aluminoferrite cements, which is explained by possible hindering by iron in the monosulphoaluminate.

Among the products of calcium aluminoferrite hydration there were also identified $2CaO \cdot Al_2O_3 \cdot 8H_2O$ and a highly ferrous solid solution of $C_4(A_{1-x};F_x) \cdot H_{19}$.

Hydration of the rest of the clinker phases. Free CaO and MgO are hydrated with the formation of portlandite, $Ca(OH)_2$ and brucite, $Mg(OH)_2$.

Because of high density of CaO and MgO crystals in clinker, their interaction with water occurs slowly and can be the cause of the inhomogeneity in the volume change and appearance of cracks in the cement paste. The alkali oxides Na_2O and K_2O, contained mainly in aluminates, aluminoferrites and glass, are dissolved in water with the formation of NaOH and KOH. The alkalis in the presence of $CaSO_4$ react with the formation of $Ca(OH)_2$ and Na_2SO_4. Sodium and potassium alkalis indirectly affect the composition of hydrated calcium silicates formed by decreasing the concentration of $Ca(OH)_2$ in water. The glassy phase of cement is hydrated actively with the formation of solid solutions of aluminoferrites, a general formula being $3CaO(Al,Fe)_2O_3 \cdot xSiO_2 \cdot (6–2)H_2O$.

Hydration of Portland cement. Hydration mechanisms of individual mineral constituents of Portland cement in the initial period after mixing with water remain the same as in the individual systems described above. However, as the content of hydrated cement and ions in the water solution increase overlapping of secondary reactions of reaction products occur resulting in the modification of primary reactions of the hydration of minerals. Therefore after a rather short period of time complex hydration products appear in the cement paste making the hydration process more complicated compared with that of individual cement

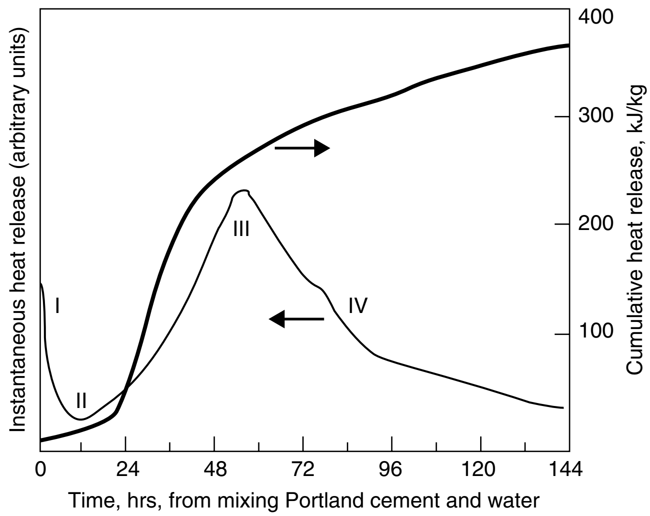

Figure 2.7 Heat evolution of Portland cement showing both instantaneous and cumulative heat evolution in the course of early hydration. Reproduced from Glasser, 2011. With permission from Elsevier

minerals. Hence, Portland cement hydration has similar hydration mechanisms but has its own features (Taylor, 1997; Glasser, 2011). The hydration process of Portland cement (Figure 2.7) similarly to the C_3S hydration process is divided into a number of stages, though the differences between individual stages of cement hydration are less distinct.

The hydration kinetics of Portland cement is not generically changed on changing its grinding fineness, however the level of maximum heat evolution increases on increasing grinding fineness (Scrivener and Nonat, 2011). The majority of research acknowledges the hydration mechanism of Portland cement offered by K.L. Scrivener (1987) and X.F.V. Taylor (1997) and shown in Figure 2.8.

Finally, in completely hydrated Portland cement the hydrosilicate gel (calcium silicate hydrate) constitutes approximately 50–60% of solid volume, $Ca(OH)_2$ approximately 20–25%, and hydrated calcium sulphoaluminate approximately15–20%.

2.5.3 Microstructure, Phases and Properties of Fresh and Hardened Cement Paste

A mixture of cement with water during the first and the second stages of hydration (Figure 2.7) is a fresh cement paste, which is a concentrated water suspension. As any viscous liquid it can be mixed with various additives and used for filling voids or storage containers with possible usage of mechanic densification. In the next stage from the beginning till the end of setting the mixture is a paste gradually losing its flowability. Any mechanic impact must be excluded at this stage. Structural–mechanical properties of cement paste improve with increase in degree of cement hydration. The yield shear stress of cement paste increases, for example from 0.01 MPa at the moment of mixture preparation up to 0.15 MPa at the beginning of setting and to 0.5 MPa by the end of setting. In further stages cement paste turns into hardened cement paste with a hundred times increased strength from the end of setting to

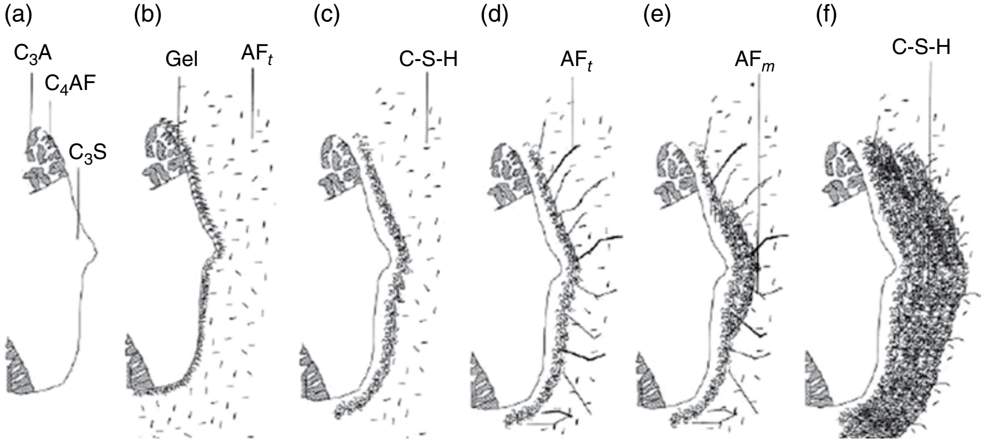

Figure 2.8 *Development of microstructure on hydration of Portland cement with time: (a) a section of polymineral grain before hydration; (b) after 10 min: part of C_3A and C_4AF forms an aluminate-containing gel on the surface, rod-like crystals of the AF_t phase emerge in gel and solution; (c) after 10 h: hydration of C_3S with formation of the outer calcium silicate hydrate phase in the net of rod-like crystals of AF_t. An approximately 0.5 μm gap remains between the surface of the grain and hydration shell; (d) after 18 h: secondary hydration of C_3A and C_4AF with formation of long rods of AF_t. The inner calcium silicate hydrate phase starts forming inside the shell of C_3S which continues to be hydrated; (e) after 1–3 days: C_3A reacts with AF_t inside the shell, forming hexagonal plates of AF_m phase. Formation of inner product decreases separation of unhydrated grain and hydrated shell; (f) after 14 days: a large quantity of inner calcium silicate hydrate is formed enough to fill the space between the grain and shell*

many years later due to continuing hydration of unreacted particles of cement clinker and polymerization of monomer SiO_4 over dozens of years to a hundred years and more.

Cement pastes are characterized by the existence of solid and pore phases, the composition and content of which change during the various stages of cement hydration.

The strength of cement paste from the moment of mixing with water is determined by the dynamic changing of so-called ‘leading’ structures. In the first stage, the content of hydration products is not high. The small amount of highly basic hydrated calcium silicate, gypsum and hexagonal crystals of $Ca(OH)_2$ cannot create a strong structure. At this stage van der Waals’ forces of self-adhesion play the determining role due to formation of the ‘leading’ tridimensional sulphoaluminate structure. They are substituted by cohesive forces due to crystal bridges in the contact zone. At the same time a coagulative structure is being formed which is thixotropic, that is it has the ability to break up reversibly during intermixing and shaking.

By the end of setting the hydrosilicate phase becomes the ‘leading’ structure and the role of cohesive bridges becomes the predominant one. During their development chemical bonding forces are most important and the cement paste transforms into a hardened state. The solid phase of hardened cement paste includes the following products of cement hydration:

- Gel of hydration products with amorphous and submicrometer crystalline structure, possessing the properties of colloids (Figure 2.9).
- Relatively large crystals of $Ca(OH)_2$ and AFm.

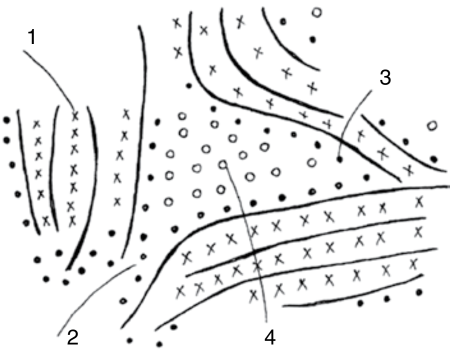

Figure 2.9 *Modified Feldman–Sereda model of cement paste (Ramachadran et al., 1981): 1, inter-crystalline pores; 2, narrow exit; 3, monolayer water; 4, inner crystalline pores*

The pore phase of hardened cement paste includes the following:

- submicrometer- and micro pores of:
  - gel (<0.1 μm);
  - capillary (from 0.1 to 20 μm);
- macropores (diameter from 20 μm to 2 mm).

Depending on the composition of the cement, initial quantity of water and technology, the porosity of the gel can be 28–40% including 7–12% due to volume shrinkage.

With the increase of hydration degree, the volume of the solid phase increases due to the chemical bonding of water and the lower density of hydration products compared with the density of the initial clinker materials. At the same time the total volume of the cement–water system is decreasing – this phenomenon is termed shrinkage. For example, in the system $3CaO{\cdot}Al_2O_2 + 6H_2O = 3CaO{\cdot}Al_2O_3{\cdot}6H_2O$ the total volume of C_3A and water is 150.11 cm^3 with shrinkage of 46.86 cm^3. Due to the fact that shrinkage is almost not decreasing the outer system volume, a vacuum is formed in the hydrated cement and under its influence pores are filled with air or water depending on the environment where the cement paste is being hardened. Shrinkage of OPCs hydrated by water over 28 days reaches 6–8 l for 100 kg of cement.

Figure 2.10 shows the approximate proportion of hydration products formed at various periods of time and the porosity of Portland fresh and hardened cement paste according to Lecher, Richartz and Schprung (Stark, 2000).

Water is present in the solid and pores of fresh and hardened cement pastes. It plays an important role in the formation of composition, structure and properties of cement paste.

In cement paste water is divided into chemically bound, adsorptive bound, zeolite water, bound by capillary forces and free water. Chemically bound water is present in stoichiometric relationships in $Ca(OH)_2$, $Mg(OH)_2$ and in crystallohydrates. Adsorptive bound water is retained by solid phase particles by van der Waals' forces and has the thickness of 2–3 molecules. Zeolite water is located in the cavities and channels of elementary lattice cells of hydrates. Capillary water is held by capillary forces in narrow capillaries of cement hardened paste. Open-ended capillaries with diameter less than 0.2 μm can be filled with water due to the sorption of water vapour from air whereas larger capillaries can be filled only on direct contact with water.

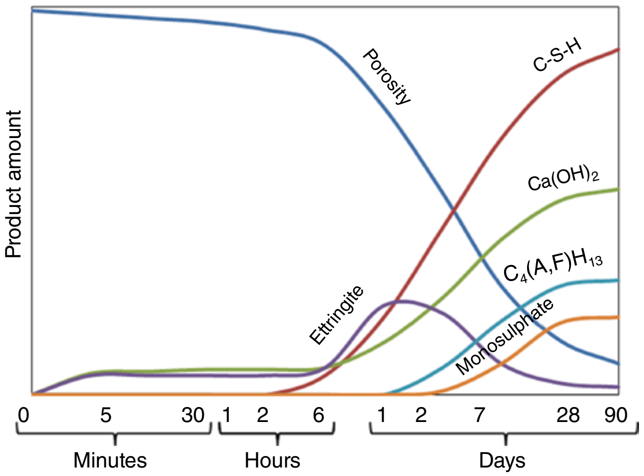

Figure 2.10 The approximate ratio between hydration products at various hardening periods and porosity

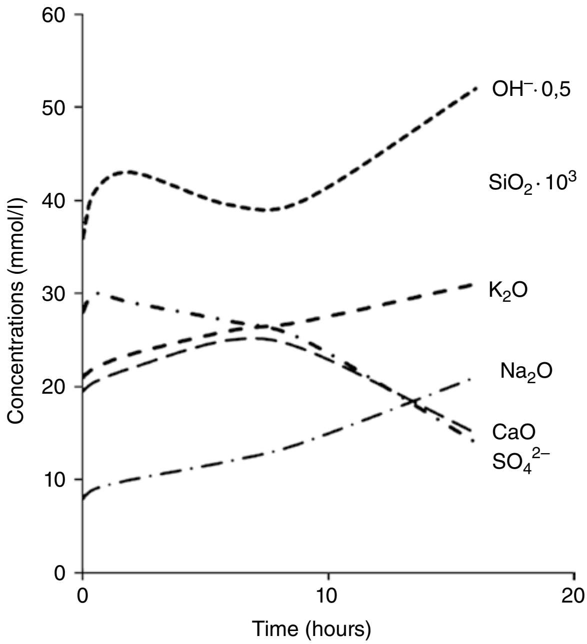

Figure 2.11 Concentration of components in pore solution of Portland cement paste with w/c = 0.5

Therefore, the pore phase of hardened cement paste can have various degrees of filled with air and pore solutions depending on the relative humidity and water availability. The pore solution is an aquatic solution of oxides and ions, being part of clinker. The concentration of oxides and ions in pore solutions changes during the cement hydration process (Figure 2.11).

The pore phase is an important component of hardened cement paste, the content and composition of which affect the properties of cementitious wasteform and its effectiveness in terms of immobilization of radioactive wastes. The properties of cement paste are characterized by a number of features which will be discussed in subsequent chapters.

The understanding of the cement hydration processes, microstructure, phases and properties of cement paste have increased in recent years due to research carried out at the nanometre-scale level and computer modelling (Kalinichev *et al.*, 2007, 2011; Pelleng *et al.*, 2008; Dolado and Van Brougel, 2011; Monasterio *et al.*, 2011; Pelletier-Chaignat *et al.*, 2011; Zhang *et al.*, 2011; Foley *et al.*, 2012; Jupe *et al.*, 2012). In recent decade blended cements with a wide range of mineral and chemical admixtures, which are more effective compared with OPC, have been developed and their applications expanded.

2.6 Interaction of Portland Cements with Water and Soil

The durability of cementitious wasteforms containing radioactive waste depends on the physical and chemical interaction of cement hydration products and radioactive waste components with ground water and soil at the location of near surface repositories.

2.6.1 Ground Waters and Their Interaction with Cement Hydration Products

Ground waters appear mainly because of infiltration. Atmospheric precipitation, river water and other kinds of water trickle through macroporous and cracked soil under the influence of gravity. Deeper they meet impervious rocks and create ground water horizons. Ground waters of different origin can be located in the crust at a depth of 1 km and more. Chemical ground water composition depends on the composition of feed waters, the composition of rock and soil with which it is in contact and always contains different amount of salts, gases, organic substances in the dissolved state and bacteria (Rakhimov and Altykis, 2005).

The main criteria characterizing the aggressivity of ground water to Portland cement hydration products are: composition of impurities; pH; mineralization; and water hardness. Ground waters contain, in different proportions, several dozens of chemical elements up to 90% of which are dissolved salts and ions (including Cl^-, SO_4^{2-}, NO_3^-, HCO_3^-, Na^+, K^+, Mg^{2+} and Ca^{2+}) and also gases (such as CO, CO_2, CH_4 and H_2S). Ground waters are divided by pH into: acid water, 1–3; slightly acid water, 4–6; neutral water, 7; mildly alkaline water, 8–10; and alkaline water, 11–14.

The classification of natural water aggressive to Portland cements is given in Table 2.4 (Glasser, 2011).

The total content of mineral substances is characterized by salinity. Ground waters are subdivided into four types depending on salinity: fresh water, up to 1 g/l; brackish water, 1–10 g/l; salt water, 10–50 g/l; salt brine, more than 50 g/l. Aggressivity of water containing carbon dioxide is determined by carbon dioxide concentration and water hardness. Water becomes hard by being in contact with soluble, divalent, metallic cations. The two main cations that cause water hardness are calcium (Ca^{2+}) and magnesium (Mg^{2+}). Water hardness in the presence of calcium and magnesium salts is measured in degrees. One degree of water hardness is equal to 0.01 g of CaO and 0.0718 g of MgO per litre of water. Water hardness can be due to the presence of carbonates, noncarbonates and both.

Table 2.4 *Classification of aggressivity of natural waters to Portland cement*

Function	Weakly aggressive	Strongly aggressive	Very strongly aggressive
pH	5.515–30–6.5	4.5–5.5	<4.5
Aggressive CO_2 (mg/l)	15–30	30–60	>60
Ammonium (mg/l)	15–30	30–60	>60
Magnesium (mg/l)	100–300	300–1500	>1500
Sulphate (mg/l)	200–600	600–2500	>2500

Carbonate hardness or carbonate alkalinity is a measure of the alkalinity of water caused by the presence of carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) anions. Carbonate water hardness is a temporary water hardness, as it is reduced while boiling water. Noncarbonated water hardness remains while boiling and shows the presence of Ca salts and Mg strong acids and is called permanent water hardness. Total hardness characterizes the total content of Ca and Mg and is the sum of temporary and permanent hardness. Depending on temporary hardness, water is subdivided into (in degrees): low hardness water, temporary hardness less than 8.4; moderately hard water, from 8.4 to 16.8; hard water, from 16.8 to 25.2; and very hard water, more than 25.2. Soft low-salt waters are typical for northern and mountainous regions where surface waters appear from ice and snow melting and rain, while deep waters which appear in piedmont and mountainous regions have high salinity and contain large amounts of dissolved gases, especially CO_2 and sometimes H_2S.

In regions with hot and dry climate the salinity of ground waters is higher than in regions with mild climate andcan reach from 100 to 600 g/l.

Corrosion types of cement-based materials are classified according to the name of aggressive substances and aggressive environmental effect mechanisms. The classification of corrosion types according to the mechanism of liquid medium aggressive influence is regarded as the most common (Moskvin, 1952). According to this classification, cement system corrosion is subdivided into three types:

1. Corrosion of the first type is connected to the dissolution of cement hydration products in water.
2. Corrosion of the second type is caused by the formation of slightly soluble salts under the influence of acids, acid gases and other aggressive substances to cement brick hydroxide.
3. Corrosion of the third type is connected to the formation of the reaction products in pores of cement paste which causes internal stress and cracking due to the large volume of the reaction products.

The cement hydration product dissolved best in water is $Ca(OH)_2$, the amount reaching 10–20% depending on the age of the cement paste. As a result, the first type of corrosion is mainly connected to $Ca(OH)_2$ leaching in soft water. The presence of the Ca^{2+}ions reduces OH, while others (SO_4^{2-}, Cl^-, Na^+, K^+) increase the dissolution of $Ca(OH)_2$. First dissolution and outwashing of $Ca(OH)_2$ takes place. $Ca(OH)_2$ not only participates in strength formation of cement paste but also is the stability regulator of other hydration products. With the reduction in $Ca(OH)_2$ concentration the basicity of hydrates decreases and they hydrolyse and dissolve in water. $3CaO{\cdot}2SiO_2{\cdot}nH_2O$ is resistant to attack of water which contains not less than 1.1 CaO g/l, and $CaO{\cdot}SiO_2{\cdot}mH_2O$ with 0.05 CaO g/l. Strength of cement paste reduces by 10% with the loss of 10% of CaO, by 25% with the loss of 20% CaO, and a loss of 33% of CaO causes complete destruction.

Calcium silicate hydrates, calcium aluminate hydrates, and calcium ferrite hydrates start decomposing on lowering $Ca(OH)_2$ content. Cement paste alkalinity is maintained at high level by continuous hydration of unreacted clinker particles in the cement paste. If clinker particles are less than 5 μm they hydrate completely during the first day, particles with sizes 50–60 μm hydrate for years to dozens of years retaining the alkalinity potential of cement stone. As a result, those cements which have specific surface area of 300–400 m^2/kg are more durable in liquid medium.

Corrosion of the second type occurs in the following forms. General acid corrosion occurs under the influence of any acid except polysilicic and hydrofluorosilicic acids. Acids interact with the $Ca(OH)_2$ of cement paste forming more soluble salts than $Ca(OH)_2$, for example $CaCl_2$:

$$\mathrm{Ca(OH)_2 + 2HCl = CaCl_2 + H_2O}$$

In addition acids also destroy calcium silicates, for example:

$$\mathrm{3CaO \cdot 2SiO_2 \cdot 3H_2O + 6HCl \rightarrow 3CaCl_3 + 2SiO_2 + 6H_2O.}$$

Magnesia corrosion takes place on the interaction of magnesium salts with $Ca(OH)_2$ which occurs in the dissolved state in ground waters. Destruction of the cement paste in this case occurs because of the exchange reaction, for example:

$$\mathrm{Ca(OH)_2 + MgCl_2 = CaCl_2 + Mg(OH)_2,}$$
$$\mathrm{Ca(OH)_2 + 2NaCl = CaCl_2 + 2NaOH.}$$

As a result $CaCl_2$ salt forms which dissolves in water and washes out from cement paste. $Mg(OH)_2$ is a water-insoluble noncrystalline mass which is not strong.

Sodium nitrate affects $Ca(OH)_2$ according to the following reaction:

$$\mathrm{Ca(OH)_2 + 2NaNO_3 + 2H_2O = Ca(NO_3)_2 \cdot 4H_2O + 2NO_3.}$$

The calcium nitrate produced is water soluble and washes out of concrete.

Carbon dioxide corrosion develops in two stages. In the first stage CO_2 forms $CaCO_3$ in water densifying the cement paste:

$$\mathrm{Ca(OH)_2 + CO_2 + H_2O = CaCO_3 + 2H_2O.}$$

Carbonization has both a positive and negative influence on cement paste (Stark, 2000). The positive influence is because:

- Density increases as the calcium carbonate formed, $Ca(OH)_2 \rightarrow CaCO_3$, is 11% larger by volume.
- Water and gas permeability decrease due to reduction of porosity by 20–28%.
- Cement strength increases up to 20–50% depending on the cement type.

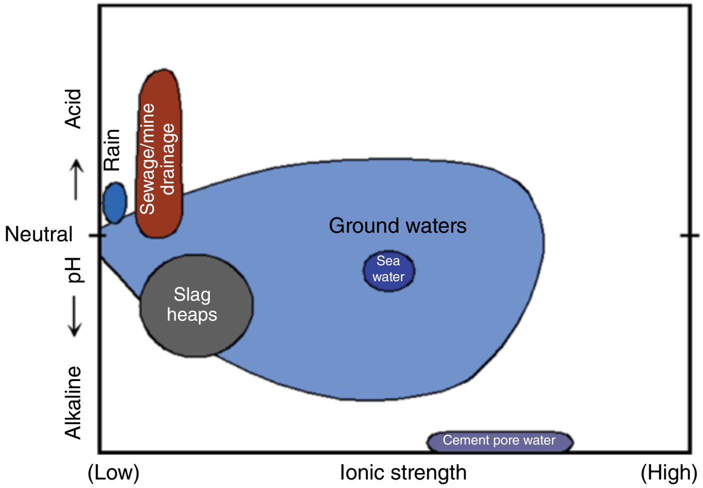

Figure 2.12 *Aggressivity of ground waters containing CO_2 Reproduced with permission from M. Ojovan*

The pH of pore water remains high until there is calcium hydroxide available and a calcium silicate hydrate phase in the cement paste. Carbonization of calcium silicate hydrate occurs according to the reaction:

$$C_xSH_y + xCO_2 \rightarrow CaCO_3 + SiO_2 \cdot yH_2O.$$

The negative influence of carbonization is due to reduction of pore water pH which leads to consequent destruction of calcium silicate, aluminate and ferrite hydrates. Figure 2.12 shows the classification of aggressivity of waters which contain CO_2 (Glasser, 2011).

On increasing CO_2 content in water degradation of cement hydrates occurs by forming calcium carboaluminates and the rearrangement of sulphates. At a certain concentration of CO_2 cement hydrates and carbonized calcium dissolve without leaching (Glasser, 2011).

The third type of cement corrosion is sulphate and salt corrosion. Sulphate corrosion results from the action of mineralized waters containing $CaSO_4$, Na_2SO_4, $MgSO_4$ on hydroaluminate of the cement paste.

The content of sulphate ion in heavily mineralized ground waters can reach dozens of thousands of microgrammes per litre. Under the influence of sulphate, gypsum forms in the concrete body, for example:

$$Ca(OH)_2 + Na_2SO_4 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O + 2NaOH,$$

which reacts with the hydrated tricalcium aluminate of the cement paste:

$$3CaOAl_2O_3 \cdot 6H_2O + 3CaSO_4 \cdot 2H_2O + 26H_2O \rightarrow 3CaOAl_2O_3CaSO_4 \cdot 32H_2O.$$

Complex reaction products with high content of crystallized water are formed as a result of this reaction (calcium hydrosulphate aluminate, termed ettringite). This process causes a 4.76 times increase in volume of reaction products. In the case of lower concentration of $Ca(OH)_2$, a highly basic form of hydroaluminate dissolves and ettringite is not formed.

It was found that ettringite formation starts in the water solution where the sulphate ion concentration is 250 mg/l or higher. A large amount is formed in water at a sulphate ion concentration of 500 mg/l.

Salt corrosion is typical for dry and hot climate when soil contains more than 1% of water soluble salts or when there is a high level of ground water mineralized (not less than 3 g/l). At certain temperature–moisture conditions several salts (NaCl, Na_2SO_4, $MgSO_4$, $MgSO_4{\cdot}6H_2O$, Na_2CO_3) turn from anhydrous and low forms into high hydrous crystal forms ($NaCl{\cdot}2H_2O$, $Na_2SO_4{\cdot}10H_2O$, $MgSO_4{\cdot}6H_2O$, $MgSO_4{\cdot}7H_2O$, $Na_2CO_3{\cdot}10H_2O$) with an increased volume larger by 11% up to 3 times. In this case induced crystallization pressure can reach up to 4.4 MPa.

Microbiological corrosion of cement materials: cement materials possess high surface activity, so they can absorb microorganisms. Germs influence the cement paste mainly by acid exudation. One of the first corroding agents is sulphurated hydrogen, formed by sulphite reducing germs. At the second stage sulphuric acid is formed which destroys cement paste. H_2S vapour from ground water of some regions acts as a substrate for germs. Thiobacillic germs convert them into sulphuric acid. One gramme of sulphur can create 3 g of H_2SO_4. Among the germs creating hydrogen nitrate one can name ammonia oxidizers and nitro oxidizers. Ammonia oxidizers produce nitrous acid which nitro oxidizers convert into hydrogen nitrate. The surface acidity of cement materials increases and the pH drops to 5–6 as a result of nitrification activity and the formation of hydrogen nitrate by germs. Calcium content in this case transfers to the solution as $Ca(NO_3)_2$ (Stark, 1988, 2000).

2.6.2 Soil and Its Interaction with Cement Hydration Products

2.6.2.1 Soil Characteristics

Rocks form the Earth's crust which is the most heterogeneous geosphere with three layers: the lower basaltic; the middle granitic; and the upper rather thin layer of sedimentary rocks. There are about 1000 rocks in the Earth's crust. Rocks are mono- or polymineral formations of more or less defined composition and structure, forming independent geological bodies in the Earth's crust.

Soil is any rock, ground or anthropogenic geological formation. The most important soils characteristics, defining their corrosiveness towards cement paste are:

- mineral and chemical composition;
- moisture content;
- grain-size composition.

Minerals are uniform in chemical composition and physical properties of the rock component parts.

By origin rocks can be divided into three groups: igneous; sedimentary; and metamorphic.

Igneous rocks form intrusive (granite, syenite and others) and effusive (basalt, diabase, pumice, tuff and others) rocks.

Sedimentary rocks are divided into three main groups in accordance with formation conditions:

1. Detrital rocks or mechanical sediments: (i) loose (gravel, sand, clay), left on the place of rock failure site or brought by water, ice (glacial sediments) or wind (atmogenic); and (ii) cemented (sandstones, conglomeration, breccia).
2. Chemical sediments (gypsum, salt, calcareous sinter): made up of destructed rock products, carried by water in solubilized condition and as a result of water expulsion.
3. Organogenic: made up of some plant and organism remains (diatomite, limestone and others).

Metamorphic rocks appeared as a result of igneous and sedimentary rock transformation in the depth of the Earth's crust under the influence of high temperatures and pressure (gneiss, marble, schist, quartzite).

The mineral and chemical composition of rocks: igneous rocks are polyminerals and they consist of different ratios and combinations of quartz, feldspar, mica and others. Igneous rocks have approximately the following composition: oxygen, 46.7%; silicon, 27.7%; aluminium, 8.1%; iron, 5.1%; natrium, 2.7%; calcium, 2.6%; potassium, – 2.6%; and the other elements do not exceed 1.4%.

In the process of sedimentary rock formation, except the minerals which the formed loose sediment was generated from, the minerals arising in this rock take part in the process of its formation (calcite, kaolin, salt and others). They have different chemical composition: aluminium silicates, carbonates, oxides, sulphates and others.

The granulometric composition of rocks: rocks are divided into monolithic massive, having destroyed massive into blocks and boulder stone, loose detrital rocks. Loose detrital rocks are the majority of intrusive and effusive rocks and separate sedimentary rocks (limestones, dolomite, anhydrite, plaster, rock salt, conglomerate, breccia, sandstones).

Loose rocks are subdivided into large, medium and small detrital rocks. Gravel which consists of gravel granules 2–150 mm in size refers to large detrital rocks. Sand with granules 0.16–2 mm in size refers to medium detrital rocks. Large and medium detrital rocks do not have granule cohesion, they are non-ductile and not waterproof.

Clay rocks, loams and sandy loams containing clay particles which are 2 μm and less in size refer to small detrital rocks. The following rocks refer to clay rocks with different clay particle content: clay, more than 30%; loams, 10–30%; and sandy loams, 3–10%. Clay rocks are the cohesive soil with well expressed plastic properties, the ability to swell in water, low water permeability and almost waterproof in wet conditions.

Soil influence on cement materials significantly depends on water solubility. Rocks are subdivided by water solubility into four groups: almost insoluble, solid igneous rocks; sparingly soluble, limestones, dolomites, limy conglomerates and sandstones; medium soluble, gypsum, anhydrite, gypsiferous conglomerates; and readily soluble, clay rocks, rock salt. Soil solubility depends on the presence of soluble elements and they are subdivided by hygroscopicity into three groups:

1. slightly soluble (silicates, phosphates and carbonates Mg, Ca, Ba, Pb; sulphates Ba and Pb; oxides and hydroxides Fe; chromates Al and Si);
2. very soluble low-hygroscopic (chlorides and sulphates Na, K, NH_4; nitrates K, Ba, Pb, Mg; alkaline metal carbonates);

Table 2.5 Degree of aggressivity of constantly moist soils

Aggressive components	Degree of aggressivity	
	Weak	Strong
Dry soil acid (ml/kg). The degree of acidity by Baumann–Gullo	>200	—
Dry soil sulphate, SO_4^{2-} (mg/kg)	2000–5000	>5000
Dry soil sulphide, S^{2-} (mg/kg)	≤100	>100

3. very soluble hygroscopic (chlorides Ca, Mg, Al, Zn, Fe; sulphates Mg, Mn, Zn, Fe; nitrates and nitrites Na, K, Al; all prime phosphates; secondary phosphate Na; oxides and hydroxides Na and K).

Soil cation-exchange capacity. Mainly cations take part in ion-exchange processes in soils as the majority of mineral and organic elements become negatively charged in water. Cations able to exchange are part of colloidal micelles around soil particles where they are on the outer surface located within the crystal lattice inter-packed space. The most spread cations in soil are: Ca^{2+}, Mg^{2+}, Na^+, K^+, H^-; less common are: Al^{3+}, Fe^{3+}, F^{2+}, NH_4^+, Li^+. Cations are classified by their activity (in descending order) as follows: Li, Na, K, NH_4, Mg, Ca, Ba, H, Al, Fe.

2.6.2.2 Soil Interaction with Cement Hydration Products

Dry soil does not have strong corrosive action on cement paste components. The majority of soils are hygroscopic capillary porous bodies and because of that adsorb moisture from air. Therefore they are typically filled with underground water to a different extent. Capillary and gravitational (percolating) water is a corrosive to cement solution which can attack cementitious materials when they form water films on their surfaces. Soil aggressivity to cements is determined by standards of aqueous medium aggressivity. Stark (2000) noted some features of soil pore solutions:

- Clay soils have low water permeability, therefore substance concentrations in soil water change slowly.
- Sand soils are water-permeable, so there can be a constant recovery of corrosive components.
- A changeable level of water increases the corrosion effect on cement paste as salts act destructively as a result of crystallization pressure in less moist zones.

Table 2.5 presents data on the aggressivity of soil components.

The degree of soil aggressivity decreases with reduction in permeability. For example, sands demonstrate acid aggressivity when water has $pH < 7$ whereas for clay it is when the water pH is < 5. Waste salts, oxides and hydroxides can affect the degree of soil water aggressivity towards cementitious wasteforms. One effective way to increase corrosive resistance of cement-based materials is to use mineral admixtures (Garcia-Calvo *et al.*, 2010; Hassani *et al.*, 2011). It is worth noting that low pH cements with silica fume as admixture demonstrate good corrosive resistance.

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3

Portland Cements with Mineral and Chemical Admixtures

The introduction of chemical and mineral admixtures is a versatile and effective way to control the composition, structure, technical and technological characteristics and economic performance of cement matrixes. Modification of various binders and materials based on them in order to improve properties of cementitious materials started 6000–7000 years ago (Vitruvius, 1936). The introduction of chemical and mineral admixtures to Portland cement and materials based on them was simultaneous with the beginning of their industrial production from the middle of the nineteenth century. Currently, the list of such admixtures includes thousands of varieties, while the production and application of modified Portland cements and materials based on it is 60–90% of the total volume of Portland cements in different countries. The largest amount of Portland cement is consumed by the construction industry in the production of concretes and mortars. Accordingly, the largest body of research, development and regulation on the use of chemicals and mineral supplements is in the application of concrete and mortars. The results of these works are of great interest in the studies on Portland cement efficiency improvement through the introduction of chemical and mineral admixtures, when used for the immobilization of radioactive wastes.

3.1 Chemical Admixtures to Control the Structure and Properties of Portland Cements

Chemical admixtures are substances mainly soluble in water and affecting basic technical and special properties of the cementitious materials (including Portland cement) and materials based on them. The diversity of substances used for structure and property modifications of cements and materials based on them required the development of classification schemes

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Ravil Z. Rakhimov, Nailia R. Rakhimova and Michael I. Ojovan.

according to composition and influence mechanisms. Currently there is no uniform classification accepted by the international community for all countries. Most countries have individual regulations on classification of chemical admixtures for cements, mortars and concretes.

Ramachandran (1995) gives a classification of chemicals, dividing them into five groups: A, water reducing admixtures; B, retarders; C, accelerators; D, water reducing admixtures and retarders; and E, water reducing admixtures and accelerators.

There are three basic types of water reducing admixtures in the ASTM C-494 Standard 'Chemical admixtures in the concrete': type A, water reducing admixtures; type D, water reducing admixtures and retarders; and type E, water reducing admixtures and accelerators.

In the British BS-5075 and Canadian CAN 3-A2662-M78 specifications standards admixtures are classified as in the ASTM Standard, with some adjustments for some requirements for the influence on properties of concrete.

In European countries, admixtures are classified according to their technological characteristics. In particular, in France and Germany, admixtures are classified as follows:

1. Changing the rheology and the air content in the mixture.
2. Modifying setting time and hardening.
3. Changing the resistance to physical and chemical effects.

Classification of chemicals according to composition and mechanism of their influence on Portland cement properties is regularly updated as studies on modification processes progress and new types of admixtures appear.

For example, over the last 30 years the following standards on admixtures for cements and concretes have been introduced in Russia:

- In 1980, GOST 24211-80, in which all the admixtures were divided into six classes according to the main effect of the action, technological features, influence mechanism, structure formation and properties of hardened pastes and concretes.
- In 1991, GOST 24640-91, in which chemical admixtures were divided into:
  - regulating basic technical cement properties: setting time regulators, accelerators increasing the strength in the initial stage, accelerators increasing the strength at 28th day aged cement, plasticizers;
  - controlling special cement properties: water-retaining, waterproofing, controlling expansion and contraction, controlling heat evolution, improving decorative properties, regulating density of the cement paste and technical cement properties for ground mortars.
- In 2003, GOST 24211-2003, in which admixtures were divided into three groups:
  - 1 – controlling properties of ready-to-use mixtures (rheological, keeping workability, porosity);
  - 2 – changing properties of cements (strength, strength development, permeability, corrosion resistance, shrinkage and expansion);
  - 3 – imparting special properties (antifreezing, waterproofing, biocidal, efflorescence).

Although different all classifications include a certain list and description of the usage of chemical admixtures for the modification of Portland cement and concretes. A typical list of admixture usages include: accelerators, retarders, plasticizers, stabilizers, density, strength and porosity regulators, increasing frost resistance, water permeability.

In some cases the chemical and mineral compositions of radioactive wastes cause acceleration of setting, whilst in other cases setting is retarded. In such cases proper control of the cement setting time is required and can be performed by the introduction of accelerators or retarders.

3.1.1 Accelerators

Introduction of accelerators to cement pastes leads to an accelerated hydration, shortening initial and final setting time, and a significant increase of early strength at normal and elevated temperatures.

Usually accelerators are electrolytes and certain organic materials such as calcium, sodium and aluminium chlorides; sodium sulphate and sodium nitrate; formate, oxalate and calcium thiosulphate; alkali hydroxides, silicates, fluorosilicates, fluorine anhydrite, various chromate compounds, oxalic acid, triethanolamine, and the formaldehyde of tartaric acid. (Millar and Nischols, 1885; Ratinov and Rozenberg, 1973; Kantro, 1975; Ramachandran, 1995; Taylor, 1997; Batrakov, 1998; Peterson *et al.*, 2011; Stabler *et al.*, 2011).

Most accelerators actively influence the hydrolysis of C_3S due to reaction with calcium hydroxide and cement minerals. As a result the amount of calcium ions and hydroxide ions in the liquid phase increases causing supersaturation and accelerating hydration product coagulation, and then crystal structure formation.

Accelerator cations are arranged according to their effect on C_3S as follows (Kantro, 1975):

$$Ca^{2+} > Sr^{2+} > Ba^{2+} > Li^{+} > Na^{+} > K^{+}$$

whereas anions follow the series:

$$SO_4^{2-} > OH^{-} > Cl^{-} > Br^{-} > J^{-} > NO_3^{-} > CH_3COO^{-}.$$

Calcium chloride is the most widely used admixture due to its availability and low cost. The first patent for its invention as an accelerator was obtained as early as 1881 (Millar and Nischols, 1885). Its introduction to cement paste at normal temperature can increase the rate of strength development up to three to four times, and at low temperatures it can be even higher.

Acceleration mechanisms of $CaCl_2$ are generalized as follows (Ramachandran, 1995):

- $CaCl_2$ causes a higher dissolution rate of cement components which leads to an accelerated hydration.
- Formation of the adsorption complex containing chloride ion on the hydratable surface of C_3A accelerates the hydration.
- $CaCl_2$ combining with aluminate and ferrite phases forms $3CaO{\cdot}Al_2O_3{\cdot}CaCl_2{\cdot}10H_2O$, $3CaO{\cdot}Al_2O_3{\cdot}3CaCl_2{\cdot}(14\text{–}32)H_2O$ complexes, which accelerates cement setting and can act as nucleation seeds for hydration of silicate phases.
- $CaCl_2$ lowers the pH of the liquid phase and promotes hydration of silicate phases.
- The calcium silicate hydrate phase formed in the presence of $CaCl_2$ has a low calcium/silicate ratio and acts as nucleation seeds, while $CaCl_2$ reacts with C_3S resulting in $CaSO_4{\cdot}2H_2O$ which accelerates C_3S hydration;

- $CaCl_2$ reacts with calcium hydroxide, which is produced during the hydration of alite and belite to form the low-basic and high-basic hydroxy salts, $Ca(OH)_2 \cdot CaCl_2 \cdot H_2O$ and $3Ca(OH)_2 \cdot CaCl_2 \cdot 12H_2O$, respectively, influencing the strength, impermeability and other properties of cements.

$CaCl_2$ promotes not only the hardening process of all types of cement, but also densification, impermeability increase, ultimate strength, porosity reduction and bleeding of cement pastes. It is also effective to use complex accelerators: $CaCl_2$, alkali salts with lignosulphonate, and so on.

Chloride-free accelerators have been developed, the efficiency of which is comparable with the effect of $CaCl_2$ such as the group of oligomeric aryl sulphonates with different structures and an average molecular weight from 650 to 1000.

Accelerators are divided according to the nature of their action into the following groups (Batrakov, 1998):

- those that do not react with cement constituents but are increasing their solubility and decreasing the freezing point of water;
- those that activate cement hydration through dispersion of its grains, destruction of silicate ingredients that increase their water solubility;
- those that accelerate cement hydration process due to exchange reactions that lead to formation of calcium hydroxide gel and reduce the freezing point of water;
- those that promote heat evolution during cement hydration and are lowering the freezing point of water.

3.1.2 Retarders

Setting and hardening retarders are introduced to the cement systems when it is necessary to extend the workability of mixtures from the start of mixing till its placing. Many organic and inorganic substances can be used as retarders:

- Unrefined sodium, calcium or ammonium lignosulphonate (containing glucose, mannose, fructose, xylose and other sugars and their derivatives, and modifiers) (Ramachandran, 1995).
- Hydroxycarboxylic acids and their salts (preferably sodium, calcium or triethanolamine salts of adipic, gluconic, tartaric, succinic, citric, malic, heptanoic acids) and their derivatives (Ramachandran, 1995).
- Sodium alkylsilyls, alkylsiloxanes nitrile trimetilenfosfonic acid; beet molasses, yeast sulphide grains (Ramachandran, 1995).
- Some polymers (esters of cellulose, derivatives of melamine and naphthalene, carbohydrate sulphates).
- Inorganic substances based on phosphates, fluorides, lead and zinc oxides, borax and magenesium salts.

There are some differences in retarder requirements throughout the world. CAN 3-A266.2-M78 (Canadian Standard Association) describes two types of retarders: the first is with moderate effect (B) and a strong retarding effect (R_1). These admixtures should reduce the water content of the mixture by not less than 3%.

According to the French standard AFNOR-NF P 18-103, retarders should provide the maximum lengthening of the initial setting time (up to 3 days), at the same time, the strength of the cement at the age of 7 days should not be less than 80% of the strength of the reference sample.

Many research studies consider that the retarder action mechanism is due to its adsorption on the $Ca(OH)_2$ nuclei and unhydrated cement grains, as well as to formation of the insoluble film of calcium salts of the retarder in cement phases, inhibiting water access for normal hydration. As a result, both the structure formation and strength development of cement paste slow down.

Most retarders are also water reducing admixtures. In particular, in the above-mentioned French standard AFNOR-NF P 18-103 it is noted that they should reduce the water content of the mixture by not less than 3%. USA, Canada, UK, Japan and Italy standard requirements for water reducing admixtures-retarders state that water content reduction should be not less than by 5% and the relative durability factor of the cement paste should be equal to or more than 80%.

Water reduction in the cement system without sacrificing the workability leads to some increase in the density, strength, water resistance and other physical properties and cement consumption reduction. In this regard, among all admixtures, plasticizers with different water reducing levels and control of rheological properties have long since taken the lead in the technologies of production and use of cement-based materials.

3.1.3 Plasticizers, Super-Plasticizers and Hyperplasticizers

One of technological requirements in cementation of radwastes is to provide high flowability of mixtures. This can be achieved by using a water/cement (w/c) ratio as high as 0.7–0.8. However, w/c = 0.2–0.23 is enough for complete cement hydration. In this regard, the excess water in the cement pastes reduces their strength and increases the porosity and permeability. One of the ways to solve these problems is to introduce admixtures, regulating the w/c ratio and rheological properties of the cement compounds.

Admixtures regulating the w/c ratio and rheological properties of cements are typically surface-active substances. The dilution effect of the cement-based mixtures by admixture introduction is called plastification. The currently accepted point of view (Batrakov, 1998) is that plasticizers are dispersants and stabilizers, creating structured films on the surface of solid phases as a result of adsorption. The main effective factors of plasticizers are: decrease of water surface tension at the interface and internal-friction coefficient of the water–cement suspension, peptization of cement floccules, smoothing the micro relief of the hydrating cement grains and increase of electrostatic repulsion of particles by changing their electrokinetic potential.

Conventional plasticizers were initially used and are still widely used. Depending on the composition their application in 0.005–0.8% by mass of cement provides 8–15% of the water requirement reduction. This group of plasticizers includes the following organic surface-active substances:

- various industrial by-products: sulphite waste liquor, offal wood during the sulphite process – technical lignosulphonates; molasses evaporated yeast bard – nutrient yeast by-products; fusion cake of dicarboxylic acids – the mixture of adipic, pentandioic and amber acids – adipic acid by-products, alkaline drain of caprolactam production;

- products of the mixture of sulphonated phenol-formaldehyde oligomers; oxidation products of phenol with hydrogen peroxide in the presence of a catalyst: acetone polycondensation with formaldehyde in the presence of an alkali catalyst, sulphate-containing waste processing of acrylate production.

Use of conventional plasticizers is accompanied by cement paste strength decrease, which limits the availability of high workability mixtures (Batrakov, 1998).

In general, the adsorption and plasticizing ability is determined by several factors, the most important of which are the length and nature of the hydrocarbon chain and the molecular weight. Based on these ideas, specially synthesized highly effective plasticizers of linear structure have been applied in recent decades. They are characterized by the presence of high molecular weight radicals and active functional groups capable of reacting with cement clinker minerals and products of their hydration. Superplasticizers can be adsorbed on different interfaces, they form spatial coagulation structures in the cement system volume and on surface layers, and thus they can be highly effective fluidizing agents of cement systems. The first patents appeared in 1935 and they have been used extensively since the early 1960s. Superplasticizers are advantageous over conventional plasticizers as they barely reduce the strength of the cements (at the same w/c ratio) and allow the water requirement to be reduced by up to 20–30%.

Superplasticizers are divided into the following groups based on their composition:

- sulphonated naphthalene formaldehyde polycondensates (SNF);
- sulphonated melamine formaldehyde polycondensates (SMF);
- sugar-free modified lignosulphonates (MLS);
- polycarboxylates and polyacrylates (P).

The following views are currently accepted depending on the mechanism of the effect of the superplasticizers: superplasticizer molecules reduce surface tension at the ‘liquid–solid’ interface, while most conventional plasticizers reduce the gas–liquid interface surface tension so that less air is entrained to the mixture in the presence of superplasticizers; superplasticizer molecules have increased dispersion effect on the cement grains with a doubling of fines and increasing binding properties of the cement; most superplasticizers affect the degree of hydration of cement less than conventional plasticizers.

SNF, SMF and MLS superplasticizers have the predominant effect of electrostatic repulsion of the cement grains. In the technical literature P group polycarboxylate ethers are called hyper plasticizers. According to their structure, hyper plasticizers are graft copolymers. In the mechanism of action of hyper plasticizers mutual repulsion of the particles and the stabilization of the suspension is provided by the dominant steric effect. This alters their effect on the rheological properties of cement systems and is related to the molecular structure of the SNF, SMF and MLS superplasticizers. They are characterized by a linear form of polymer chain, however hyper plasticizers have cross links and a complex two- or three-dimensional shape. Cross components provide volume containment around solid particles and prevent their aggregation and cause their mutual repulsion. Hyper plasticizers differ from superplasticizers in having a stronger plasticizing effect (e.g. reducing water requirement by more than 30%).

Depending on the synthesis conditions, polycarboxylates can be obtained with different lengths of the lateral polyester chains and materials are created with different steric effect and anionicity ratios (Batrakov, 1995; Moratti *et al*., 2011). When using all types of plasticizers it is necessary to consider that their effectiveness depends strongly on the chemical and mineral composition of cement.

Almost every country has developed, manufactured and sold a wide range of plasticizers of various water requirement reducing level for various applications (Ramachandran, 1995; Taylor, 1997; Batrakov, 1998). Consequently, it seems reasonable to briefly characterize them here. The use of plasticizers in cement matrixes for radwaste immobilization is a poorly studied but promising area capable of contributing to the improvement and increase in the volume content of various radioactive wastes.

3.1.3.1 Air-Entraining Agents

Frost resistance is an important requirement of cementitious wasteforms. At negative temperatures the pore solution turns into ice which has a larger volume compared with the initial water which causes internal pressure. On cyclic freezing this can result in the destruction of the capillary walls and crack development (Klieger, 1966, 1978; Powers, 1968; Ramachandran, 1995; Batrakov, 1998; Romano *et al*., 2011).

One of the effective ways to improve frost resistance of cements is to introduce air entraining agents. These admixtures belong to surface-active substances characterized by a hydrophobic effect and at a dosage of 0.01–0.001 wt% form 3–5% conditionally closed pores which are 10–30 μm in diameter. These act as dampers effectively absorbing ice-induced pressure.

Air-entraining agents are classified chemically into the following groups: (i) pine tar utilization salts; (ii) lignosulphonates; (iii) petroleum acid salts; (iv) protein utilization salts; (v) organic sulphonic acid salts; and (vi) synthetic detergents.

The most widely used is the first group, known as neutralized vinsol, the soda neutralized mixture of phenols, acids and other substances produced in the form of waste resulting from purification and turpentine extraction from the pine tar process. The second and third groups are by-products, respectively, of the pulp and paper industry and the petroleum industry. The fourth group is produced from animal waste. The fifth group is obtained by the recycling process of soap making and plant oils. The sixth group is produced from alkylaryl sulphonates, which are petroleum residuals fused with benzene, and then sulphonated and neutralized to produce soluble chemicals.

In the list of air-entraining agents there are substances that are used as conventional plasticizers. In essence, the majority of air-entraining agents demonstrate also a water-reduction effect. In particular, products based on sodium salts of mono-and dicarboxylic acids, cyclohexanol and cyclohexanone (alkaline water discharge of caprolactam production), the oxidation product of dephenolic resin from wastewater, the neutralization product of the acid sludge and organic-silicon compounds are used as both plasticizers and air-entraining agents.

Air-entraining agents are long chain molecules with polar groups at one end and apolar groups at the other. They are concentrated at the air–liquid phase interface with polar groups in the liquid and apolar elements outside it. Inside, the surface of air bubbles consists of a hydrophobic material, formed by apolar units, which act as a barrier to water penetration and ensure their stability during agitated mixing and packing.

The slight and expected decrease in the strength of cements through air entrainment is almost offset by their water requirement reduction. It is also important that air-entraining agents reduce water permeability of cement materials.

3.1.3.2 Defoamers

It is known that highly dense materials, including cement pastes, demonstrate improved immobilization properties. On near-surface disposal of radwastes at depths of 10–15 m and more, soils and materials are not frozen during the winter. The use of most types of plasticizers is accompanied by air entrainment. To minimize the effect of air entrainment defoamers and air-entraining admixtures can be used. Such admixtures have various chemical bases: hydrocarbons, polyglycols and polysiloxanes.

3.1.3.3 Admixtures for Cement Paste Densification

Chemical densifiers include ferric sulphate, nitrate and chloride, aluminium sulphate, calcium nitrate, ammonium sulphate, polyamine resin, fatty epoxy resins and carbamide resins. Introduction of the densifiers as 0.5–1 wt% provides higher water resistance and increase in strength up to 20% of cement hardened pastes. Introduction of inorganic salts leads to intensification of the cement mineral hydration processes and increase in gel-like phase content, which clogs up the capillaries and sedimentation pores and channels. During the structuration of cement paste, resin admixtures fill the capillaries and pores, improving the strength and impermeability of cement paste.

3.1.3.4 Water-Retaining Agents and Stabilizers

At high w/c ratio concrete segregation (unmixing) may occur during transportation and placement, and water bleeding during the setting process. To eliminate these processes hydromodifiers are used, which are both water retaining and stabilizing.

Such admixtures include polyoxyethylene, fatty epoxy resins, latex emulsions, starch ethers, cellulose ethers and cellulose esters: methylcellulose, carboxymethyl cellulose and its sodium salt, hydroxyethylcellulose, oxyethylated and hydroxypropylated methylcellulose.

With 0.2–0.4 wt% admixture content the cement paste retains up to 97–99% of water. Introduction of the hydromodifiers reduces the fluidity of cement pastes by reducing the amount of free water. Admixtures release the retained water for continuing hydration of the unreacted portion of the cement grains.

3.1.3.5 Water Absorption and Water Permeability Reducing Admixtures

Most of the corrosion processes in materials take place in a moist environment. In order to improve corrosion resistance of cementitious materials water-repellent agents are used to reduce water absorption and water permeability due to decrease of the wettability of walls and capillaries of cement paste. The most frequently used water-repellent admixtures are: calcium and ammonium salts of fatty acids, such as stearates; ammonium stearate aqueous dispersion, butyl stearate, some vegetable and animal oils and emulsions based on tall or soybean oils, heavy mineral oils, paraffin waxes, bituminous emulsions and methylsiliconate solutions.

3.1.3.6 Biocidal Admixtures

On destruction of barrier protection cementitious wasteforms are exposed to aggressive action of waste products of microorganisms. Under bacterial attack initial aggressive agents are organic and mineral acids formed as a result of biochemical processes. These acids react with thardened cement paste and gradually destroy it. Antibacterial, fungicidal and insecticidal agents are used to prevent adverse biological corrosion. Such admixtures include polychalogenated phenols, sodium benzoate, benzoalkonium chloride, acetic-arsenious and arsenate copper (Ramachandran, 1995) and poly polyhexamethylene guanidine phenol (Varlakov *et al.*, 2001; Gorbunova *et al.*, 2011).

3.1.3.7 Complex Chemical Admixtures

The above mentioned admixtures allow controlling a group of properties of cement pastes for example acceleration or deceleration of setting and hardening, water requirement, workability, air entrainment, stabilization, sealing, and so on. However, almost each admixture improves some performance properties but reduces other performance characteristics. For example, introduction of plasticizers reduces the water requirement of cement pastes, but extends the setting and hardening times. Introduction of air-entraining admixtures increases the freeze–thaw durability of cement-based materials but reduces their density and strength. In recent decades production and use of complex chemical admixtures has progressed, with positive properties being used and drawbacks of individual admixtures being reduced. The main advantages of the complex admixtures are:

- multifunctionality of their effects, that is, the ability to simultaneously cause several effects, such as increasing the workability and acceleration of the hardening;
- they simultaneously improve the rheological properties, accelerate hardening and improve water resistance and waterproofing.

A wide range of complex admixtures is known, which allow to simultaneously control the structure and the set of functional properties of cement compositions.

3.2 Mineral Admixtures in the Control of the Composition, Structure and Properties of Cements

Portland cement has been and remains, for the foreseeable future, the main hydraulic binder both in the construction industry and in the immobilization of radioactive wastes. However, its production is associated with high consumption of natural minerals, energy resources and significant amounts of polluting emissions. To produce 1 t of Portland cement more than 1 t of limestone, 200–300 kg of fuel and more than 100 kW of electrical energy is required. In addition its production is a major source of up to 1 t of carbon dioxide being released into the environment, of up to 9.5 kg of nitric oxides, and of a significant amount of dust (Ferronskaya *et al.*, 2005). Environmental pollution by waste and by-products of continuously developing industrial activity in general has led to the world community understanding that humanity has reached the limits of its growth. In 1992, in Rio de Janeiro at the UN Summit on the Environment the ‘Agenda for the XXI Century’ was adopted, in which the unlimited capacity of industrial activity was replaced by the conception of ‘sustainable development’ of the world civilization (United Nations, 1991). It is based on the principles of resource and energy efficiency and environment protection from the by-products and biowastes. It has led to the revision of the future strategy of energy-intensive and material-intensive industries and the requirements for certain materials and technologies, including Portland cement (Rakhimov *et al.*, 2009).

The sustainable development problem in production and use of hydraulic binders is currently being dealt with in two ways (Pricc, 2007; Rakhimov and Rakhimova, 2013):

1. Increase in production and use of Portland cement with a low content of clinker and high content of mineral admixtures of natural and anthropogenic origin.
2. The development and production of clinker-free binders as an alternative to Portland cement, the production of which is not connected with preferential consumption of natural raw materials and high energy, and by-product emissions into the environment.

Mineral admixtures are now introduced as fillers in composite materials based on a wide range of materials (Figure 3.1), while ensuring their economic and technical efficiency (Figure 3.2) (Rakhimov and Rakhimova, 2011). Figure 3.3 shows the system of factors that determines the structure and properties of filled materials (Rakhimova, 2010).

3.2.1 Classification of Mineral Admixtures for Cements

A wide range of supplementary cementitious materials (SCMs) is subdivided into a number of types accounting for a variety of characteristics.

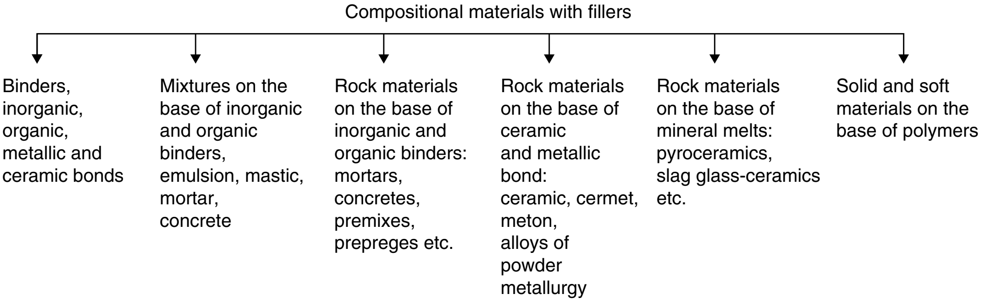

Figure 3.1 Compositional materials with fillers

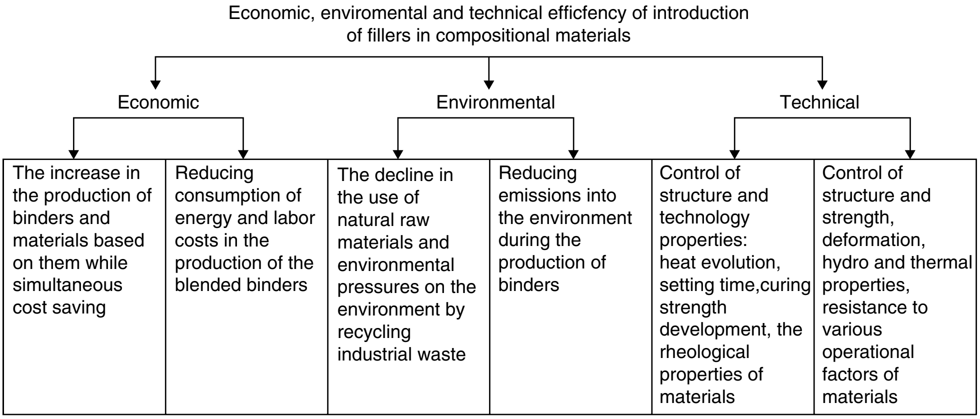

Figure 3.2 Economic, environmental and technical efficiency of introduction of fillers in compositional materials

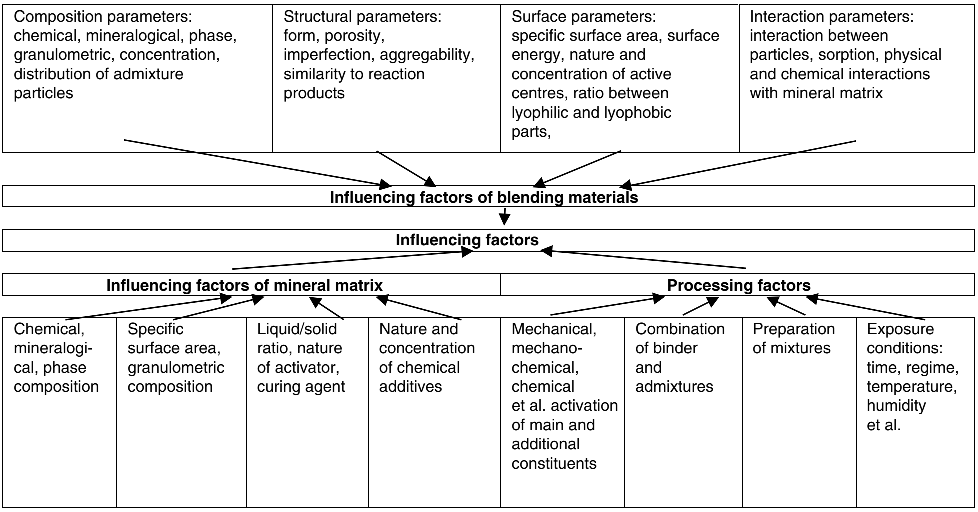

Figure 3.3 *System of the influencing factors for compositional materials*

3.2.1.1 The Classification of SCMs by Their Origin

By origin SCMs are classified as:

- natural igneous (volcanic ashes, tuffs, pumice, trasses, glasses, etc.);
- natural of sedimentary origin (diatomites, tripoli, shale, zeolites and zeolite-containing rocks, etc.);
- industrial wastes (metallurgical slags – furnace, steel, nonferrous metals, silica fume, by-products of mining and mineral processing industry – igneous and aqueous rocks; ashes, ash slags and slags from fuel-burning power plants; rice hull ash, sugar-cane ash, slat ash, peat ashes; industrial mineral wastes of constructional materials and demolition of buildings and structures, etc.);
- artificially produced SCMs such as burnt clay and loam and metakaolin.

SCMs of natural origin and those considered industrial wastes are typically fine-dispersed materials resulting from crushing and grinding of raw materials or formed as powdered waste products of different industries.

The artificially obtained SCMs result from heat treatment and chemical modification of certain types of natural and raw waste materials followed by crushing and grinding or by synthesis of fine-dispersed materials.

Each mentioned admixture represents a group of materials which differ by chemical and mineral composition and activity.

3.2.1.2 The Classification of Mineral Admixtures by Activity

The most known classification of mineral admixtures is by dividing them into inert and active SCMs (RILEM, 1988; GOST 24640-91, 1991). Active SCMs are then divided into hydraulic and pozzolanic. Inert mineral admixtures are substances which do not form reaction products with cementitious properties. Active SCMs do form such reaction products (Mehta and Gjørv, 1982).

Pozzolanic SCMs have no CaO in their composition. When mixed with water they cannot themselves form cementitious reaction products. When interacting with Portland cement, with the production of CaO during C_3S and β-C_2S hydration, they form additional reaction products with cementitious properties. Hydraulic SCMs have their own reserve of CaO, which together with the hydration products of cement, is involved in the formation of the cement paste becoming solid during its interaction with SiO_2, Al_2O_3 and Fe_2O_3 admixtures. Such admixtures can be classified as latent or potential cements (Taylor, 1997). However this distinction is relative since all kinds of mineral admixtures, to a varying degree, affect the structure and properties of the cements and are, again, to a varying degree, polyfunctionally active (Rakhimova, 2010).

Reference to some mineral admixtures as 'inert' limits their importance in the structure and properties formation process of systems filled by them and the efficiency of their use. There has been criticism of the division of mineral admixtures into 'inert' and 'active' even for concrete (Vinogradov, 1988). This criticism is justified for finely dispersed mineral admixtures, most of which are not inert, and their interaction with the cement hydration products is determined by the chemical activity, physical–chemical activity and surface area (Mchedlov-Petrosian, 1988).

In this connection it is more reasonable to subdivide mineral admixtures into three main groups as follows (Rakhimov and Rakhimova, 2011):

1. Physically active, which do not form reaction products with cementitious properties but participate in the formation of the structure and properties of binder systems. A classic example of a physically active mineral admixture is quartz sand with a surface area of 200 m^2/kg. It is involved in the structure formation of the cement system as the nucleation site for the growth of cement hydration products. On filling of the cement system up to 25–30% this admixture forms its skeleton, giving the system an increased compressive strength due to the 'tightness'. The chemical activity of the thin (30–40 nm) amorphized layer produced on grinding to achieve a surface area up to 200 m^2/kg can be neglected because of its miniscule volume.
2. Physically and chemically active mineral admixtures, which take part in the structure formation of the cement system so that a certain fraction of their particles chemically reacts with hydration products of the cement to form a binding agent, and some elements remain in the system as just a physical filler. An example of such a substance is quartz sand grinded up to 300–1000 m^2/kg fineness.
3. Chemically active mineral admixtures, which take part in the structure formation of the cement system with their complete interaction with cement hydration products to form an additional binder. Examples of such material are silica fume and ground quartz sand having a specific surface of 2000 m^2/kg or more.

3.2.1.3 Classification of Fillers by the Energy Potential, Nature and Concentration of the Superficial Centres, and Adsorption Abilities

Mineral admixtures are subdivided into five groups depending on their energy potential (Rybev *et al.*, 1987):

1. Fillers from ultra-acid and acid rocks with high negative potential due to the presence of significant amount of adsorption centres on particles in the form of ions (quartz, granite, etc.).

2. Fillers from average igneous rocks and minerals with high negative potential due to the presence of adsorption centre particles O^{2-} and monovalent cations K^+, Na^+ (orthoclase, albite, etc.) on the surface.
3. Fillers from average, basic and ultrabasic igneous rock with lowered negative potential due to the presence of a significant amount of adsorption centres on particles in the form of O^{2-} and cations of various activity, K^+, Na^+, Ca^{2+}, Al^{3+}, Fe^{3+} (anorthite, basalt, etc.).
4. Fillers of basic sedimentary rocks with high positive potential due to the presence of a considerable amount of adsorption centres on particles in the form of the cations Ca^{2+} and Mg^{2+} (limestone, dolomite, etc.);
5. Fillers with mainly neutral surfaces (graphite, talc, etc.).

A prognostic assessment of igneous rock filler hydraulic activity increase can be done based on its mineral structure (Bajenov *et al.*, 2006):

- for rocks of granite-like structure: alkaline granites – alkaline syenites – quartz syenites – syenites; diorites – gabbro-diorites – gabbro (gabbro-diabases);
- for rocks of granite-porphyric structure: alkaline granite porphyrins – alkaline syenite porphyrins – granite-porphyrins – syenite-porphyrins; quartz-diorite-porphyrites – gabbro-porphyrites;
- for rocks of porphyric or glassy structure: dacites – orthoclase basalts – andesites – andesite-basalts – basalts.

The energy potential, concentration of surface charge centres, adsorption ability and physical, physical– chemical and chemical fillers activity increase with increase in their dispersion.

3.2.1.4 Classification of Mineral Admixtures by Dispersion

Admixtures are subdivided into the following groups depending on mineral specific surface as follows:

- low dispersion – 30–200 m^2/kg;
- average dispersion – 200–500 m^2/kg;
- high dispersion – 500–1500 m^2/kg;
- ultradispersion – 1500–6000 m^2/kg;
- nanodispersion – 10 000–100 000 m^2/kg.

The specific surface energy rises from about 40 for low dispersion to 1 MJ/kg for nanodispersion. Depending on mineral admixture dispersity, the size of particles decreases from 0.16 mm for low dispersion to 1 nm for nanodispersion and the number of particlesin 1 m^3 increases from 5×10^6 to 2×10^{24}, respectively.

The effect of mineral admixtures on structure and property formation processes of cement systems also depends on the form of the particles, for example cubic, spherical, prismatic, lamellar or needle-like.

3.2.1.5 Classification of Mineral Admixtures by Efficiency in Economy of Cement

Mineral admixtures are subdivided into four groups based on degree of efficiency in economy of cement E_a (Vysotsky, 1994):

- high efficiency with $E_a > 70\%$;
- average efficiency with $E_a = 40 \ldots 70\%$;

- low efficiency with E_a = 10–40%;
- ineffective with E_a < 10%.

3.2.2 Portland Cements with Mineral Admixtures from Natural Rocks and Minerals

One of the most spread mineral admixture is quartz sand, which is easily accessible and has almost unlimited stock in many countries.

Quartz sand, ground to fineness of 200 m^2/kg, is considered a classic 'inert material'. By introducing 25–30% quartz sand, the strength of a cement hardened paste slightly increases. At higher content the strength decreases proportionally to the increase of the admixture content. According to Volgensky (1986), the production of blended cement obtained by joint grinding of Portland cement clinker with quartz sand up to specific surface of ≥250–350 m^2/kg is considered effective as the jointly grinded blended cement demonstrates the same properties as 'pure' cement.

Figure 3.4 (Babkov *et al.*, 2002) shows data of the influence of quartz filler dispersion on the strength of hardened cement pastes.

With the increase in dispersion of ground quartz sand up to 580–1330 m^2/kg the strength of a cement hardened paste increases by 15–100% depending on duration of hardening. This is explained by the increase of pozzolanic activity of quartz sand. It is known that on grinding the surface of quartz sand particles become amorphous at a depth of 7–40 nm and the volume of the amorphous phase increases with increaing dispersity (Babkov *et al.*, 2002).

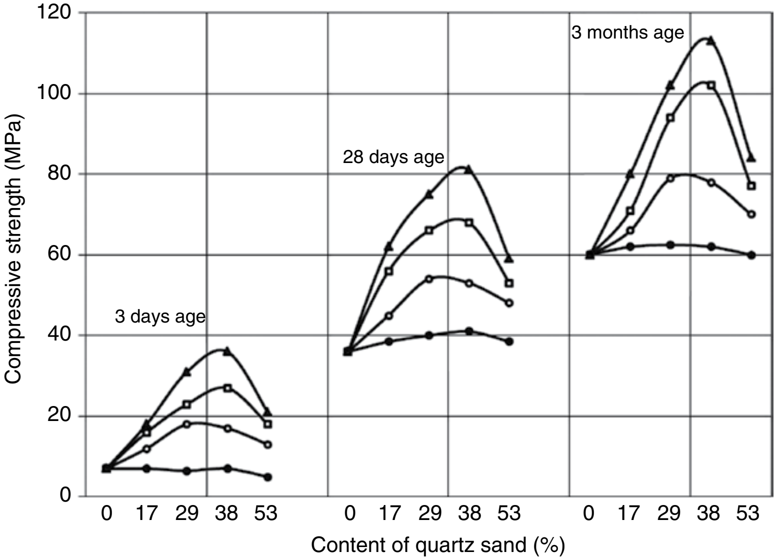

Figure 3.4 *Strength of cement pastes (w/c = 0.3) with admixture of quartz sand depending on dispersity of quartz sand: (●) quartz sand (0.3–2.5 mm); (○) quartz filler (specific surface area 5800 cm^2/g); (□) quartz filler (specific surface area 9500 cm^2/g); (△) quartz filler (specific surface area 13300 cm^2/g). Reproduced with permission from Babkov et al., 2002*

Introduction of ultradisperse quartz sand leads to cement hydration heat evolution decrease (Phung, 2011). With increase in quartz sand dispersity from 240 to 1300 m^2/kg water penetration of cement hardened pastes decreases (Wang *et al.*, 2011).

Mineral admixtures from igneous eruptive rocks at dispersion of 380–570 m^2/kg also lead to an increase in strength characteristics of cement pastes depending on their content from 20 to 100% (Bajenov *et al.*, 2006). The most effective are mineral admixtures from perlite, barite, granite, basalt porphyrite and nepheline syenite.

Production of blended cements with mineral admixtures from quartz sand, and intrusive and effusive rocks is associated with high energy expenditure for grinding. Therefore production and application of blended cements with mineral admixtures from rocks of lower cost for grinding and higher activity is economically expedient. Pozzolanic natural admixtures belong to such materials: volcanic ashes, tuffs, glasses, pumice, trasses, perlites, the burnt earth, zeolites and zeolite containing rocks. They have 70–90% silica and alumina highly reactive to lime (Sersale, 1980; Snellings *et al.*, 2009). Reactivity of such admixtures is defined by their mineral and chemical composition (Rakhimov *et al.*, 1991; Erdem *et al.*, 2007; Mostafa *et al.*, 2010). Introduction of pozzolanic additives in cements improves their density and water resistance, reduces water separation, increases fracture strength, corrosion stability and reduces efflorescence. A special place among mineral admixtures is occupied by carbonates. They belong to inert additives as they show neither hydraulic nor pozzolanic activity. At the same time they show physical and chemical activity. In the literature (Timashev and Kolbasov, 1981; Dhir *et al.*, 2007) it is noted that application of carbonate rocks reduces cement segregation, bleeding and heat evolution, increases water and frost resistance and the resistance of cement-based materials to the influence of sea water. The influence of admixtures of limestone is explained by their chemical interaction with hydration products of aluminium containing clinker phases which is accompanied by favourable changes in morphology of the crystal hydrates formed (Timashev and Kolbasov, 1981; Nocuń-Wczelik and Łój, 2011).

It has been found that the complex compounds of $3CaO{\cdot}Al_2O_3{\cdot}CaCO_3{\cdot}11H_2O$ are formed on the carbonaceous substrate in the system of a continuous series of solid solutions of $3CaO{\cdot}Al_2O_3{\cdot}0.25CaCO_3{\cdot}0.75\ Ca(OH)_2{\cdot}12H_2O$; in particular $3CaO{\cdot}Al_2O_3{\cdot}3CaCO_3{\cdot}32H_2O$ formation is revealed. At present blended cements with mineral admixtures from limestone are manufactured industrially. The possibility of production of cement with dolomite admixture (Schöne *et al.*, 2011) and dolomitized limestones (Rakhimov *et al.*, 1995) is also considered. Rakhimov *et al.* (1995) have revealed that the efficiency of carbonate rock mineral admixtures decreases with the dolomite content increase. The mineral admixtures listed above can be obtained on crushing and grinding materials of the corresponding rocks from the mining and processing industries. However, the largest part of blended cements is made with mineral admixtures from waste products of other industries.

3.2.3 Portland Cements with Mineral Admixtures from Wastes of Various Industries

Mineral admixtures from waste products find extended applications for cement modification. This is connected not only with their availability in large quantities and at low prices compared with clinker but also with the simultaneous solution of problems of sustainable production and application of cement in terms of resource and energy efficiency and environment protection from contamination by waste. More than 30 years ago in a United

Nations Expert Group report it was predicted that by the middle of the twenty-first century up to 50% of raw materials required will be covered by using industrial wastes (Leontyev, 1979). The reduction of natural raw material consumption in production and application of Portland cement is now 20–30% due to industrial wastes use. The use of mineral admixtures from waste is accompanied by an increasing amount of analytical and research work (Volgensky and Popov, 1961; Lea, 1971; Volgensky *et al.*, 1984; Lothenbach *et al.*, 2011; Scrivener and Nonat, 2011; Deschner *et al.*, 2012).

Ashes resulting from burning of coal and the processing of some agricultural crops find effective application as SCMs. Fly ashes trapped on purification of waste gases by cyclones and electric filters while burning coal at power stations are used in considerable quantities as SCMs.

Fly ashes are subdivided depending on chemical composition by standard ASTM C618 (2003) into two classes:

- Class F – (SiO_2 + Al_2O_3 + Fe_2O_3) > 70%, obtained on burning anthracite or bituminous coals;
- Class C – 70% > (SiO_2 + Al_2O_3 + Fe_2O_3) > 50%, obtained on burning brown coal.

The technical literature in many countries defines Class F fly ashes as acid pozzolanic admixture with CaO content up to 5%, and Class C fly ashes as basic, including ashes which have hydraulic activity with CaO content from 10 to 35%. Fly ashes consist mainly of spherical smooth solid grains of aluminosilicate glass, which provides their low flowability in cement pastes.

Rice husk ash is used as a SCM in cement in Southeast Asian countries. This type of ash consists of silica in cellular non-crystalline form with a high specific surface (50 000–60 000 m^2/kg) (Mehta and Pitt, 1976) and therefore it showshigh pozzolanic activity (Mehta and Pitt, 1976). Sugar cane bagasse ash was identified as an expedient SCM (Cordeiro *et al.*, 2011). Waste products of the metallurgical industry and silica fume are extensively used as SCMs.

Metallurgical industries produce blast furnace, ferroalloy and steel slags, and nonferrous slags. The blast furnace slag obtained by fast cooling of melt at 1400–1500 °C by water and by water and air is the most used hydraulic admixture in Portland cement (20–95%). As a result of fast cooling the blast furnace slag contains ≥90% of glassy phase which on fine grinding is an effective SCM. Unlike high-calcium fly ash blast furnace slag can contain increased CaO content. The degree of hydraulic activity of slags is to a certain extent characterized by the modulus of basicity:

$$\mathrm{Mo} = \frac{\left(\mathrm{CaO} + \mathrm{MgO}\right)}{\left(\mathrm{SiO_2} + \mathrm{Al_2O_3}\right)}$$

and by the modulus of activity:

$$\mathrm{Ma} = \frac{\mathrm{Al_2O_3}}{\mathrm{SiO_2}}.$$

Depending on the modulus of basicity, slags are basic with MO > 1, neutral when MO = 1 or acid when MO < 1.

Depending on the chemical composition slags can be:

- siliceous, $SiO_2 > 40\%$,
- aluminous, $Al_2O_3 > 15\%$,
- calcareous, $CaO > 50\%$;
- magnesia, $MgO > 10\%$;
- ferrous, $FeO > 5\%$;
- manganese, $MnO > 5\%$;
- titaniferous, $TiO_2 > 5\%$;
- sulphurous, $CaS > 5\%$.

Hydraulic activity of blast furnace slags as a rule increases with increasingmodulus of basicity and activity, and with increasing specific surface area. Slow cooled blast furnace slags are weak 'pozzolans'.

Steel and non-ferrous slags are applied as SCMs in far smaller volumes compared with granulated blast furnace slag but studies of possible expansions of their application have been conducted (Bignozzi *et al.*, 2011; Li *et al.*, 2011).

White carbon containing highly reactive amorphous silica can be used for production of high-performance, cement-based materials with low permeability (Cheng-yi and Feldman, 1985; Batrakov, 1998; Loser *et al.*, 2010). It is produced by gas phase deposition as a by-product with a very high surface area of 20–30 m^2/g in the production of ferrosilicon alloys or silicides.

According to Scrivener and Nonat (2011), Portland cements containing ≥24% of silica fume fully bind over time with the $Ca(OH)_2$ of cement paste, which contains more small pores and less large capillary pores compared with Portland cement without additives.

3.2.4 Portland Cements with Synthetic Mineral Admixtures

Clays do not have pozzolanic properties until the crystal structure of aluminosilicate minerals turns into an amorphous or disordered state on thermal treatment (Mehta, 1995). According to Mehta, thermal treatment production is unprofitable because of significant energy consumption during the process. However, there has been a recent increase in the number of studies on SCM production by burning clay at temperatures of 600–800°C (Castillo *et al.*, 2011; Fernandez *et al.*, 2011; Martirena *et al.*, 2011). Metakaolin produced on burning clay containing kaolinite is a highly active pozzolanic admixture and is increasingly used. The dosage of metakaolin may be 2–2.5 times less than the content of microsilica. In particular, the addition of 1.5–2.5 wt% metakaolin to Portland cement is enough to significantly increase water resistance of the cement compositions (Calardone *et al.*, 1994; Gleize *et al.*, 2007; Zakharov and Kalachin, 2007).

The addition of components capable of reacting with each other to form new hydrate phases and serving as nucleation sites for crystallization of the reaction products is effective for modifying cement systems. These are so-called crystalline components, crents (Kuznetsova *et al.*, 1989). One of the suggested crents added in amounts of up to 10wt%into cement contains amorphous oxide or silicon acidic hydrogen, aluminium hydroxide and aluminium sulphates. To increase the strength of cement paste a powdered sulphoaluminate clinker is added into the cement in an optimal amount.

In the field of research and modification of cement materials which aims to improve their physical and technical properties, the application of nanotechnology has become a key theme in the last decade (Tretyakov and Goodilin, 2009; Raki *et al.*, 2010; Schmidt *et al.*, 2013).

The effectiveness of nanomodification of cement materials is related to the state of research of the atomic to nanoscale and microscale levels of cement hydrates, primarily calcium silicate hydrate, which forms up to 60 vol% of paste (Shahsavari *et al.*, 2011; Wu, 2011). This results in an effective manipulation of the nature of the derived materials. There are two areas of modification of cement systems by nanoparticles:

1. A preliminary synthesis of the particles followed by subsequent addition to the mixture.
2. A purposeful cultivation of nanoparticles in the hardening system which are needed to modify the structure and properties (Korotkikh *et al.*, 2009).

To date, the modification of cement systems has shown mainly the development of the second variant. Current studies are devoted to use of nanoparticles, particularly SiO_2 and Fe_2O_3 (Korpa and Trettin, 2005), $Ca(OH)_2$ (Sato *et al.*, 2007), $CaCO_3$ and zeolites (Raki *et al.*, 2010). It was found that these nanoparticles have a positive effect on the properties of cementitious materials. It has been established (Lee *et al.*, 2009) that nanoparticles of TiO_2 accelerate the process and increase the degree of hydration. A significant increase in strength under pressure and bending, hardness, elasticity, crack resistance and water resistance of cement materials is achieved by addition of single-layer carbon and multilayer nanotubes (Raki *et al.*, 2010; Chen *et al.*, 2011; Gabidullin *et al.*, 2013). The best results indicate a 50% increase in compressive strength and 227% increase in Young's modulus after addition of multilayer carbon nanotubes. At the same time, the addition of nanoparticles and carbon nanotubes is affected by the need for their uniform distribution in cement; the required optimal technology is being sought. Therefore, despite the apparent effectiveness of modifying cement materials, conventional regulation documents are not yet in place.

In many countries cements with mineral microdisperse admixtures are produced according to the standard EN 197-1:2000. The 27 products in the family of common cements are listed in Table 3.1. This standard regulates the requirements for cements containing 1 cement without admixtures, 20 cements with one type of mineral admixtures and 6 cements with hybrid mineral admixtures.

In the past decade there has been an increase in research on developing new effective varieties of cements with hybrid mineral and organic-mineral admixtures.

3.2.5 Portland Cements with Hybrid Mineral and Organic-Mineral Admixtures

3.2.5.1 Portland Cements with Hybrid Mineral Admixtures

Addition of hybrid mineral admixtures can be accompanied by their synergistic effect on the hydration processes and properties of cementitious materials.

During hardening due to shrinkage there can be crack development in cement materials. Admixtures based on calcium sulphoaluminate and limestone, gypsum and limestone, monosulphate and gypsum are used to avoid this phenomenon (De Weerdt *et al.*, 2011; Giergiczny *et al.*, 2011). The most widely used admixture consists of 30% C_4A_3S, 50% $CaSO_4$ and 20% CaO.

Table 3.1 *The 27 products in the family of common cements (EN 197-1:2000)*

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

(*continued*)

Table 3.1 (*continued*)

Main types	Notation of the 27 products (types of common cement)		Composition [percentage by mass[a]]										
			Main constituents										Minor additional constituents
						Pozzolana		Fly ash			Limestone		
			Clinker K	Blast-furnace slag S	Silica fume D[b]	Natural P	Natural calcined Q	Siliceous V	Calca-reous W	Burnt shale T	L	LL	
	Portland-limestone cement	CEM II/A-L	80 to 94	–	–	–	–	–	–	–	6 to 20	–	0 to 5
		CEM II/B-L	65 to 79	–	–	–	–	–	–	–	21 to 35	–	0 to 5
		CEM II/A-LL	80 to 94	–	–	–	–	–	–	–	–	6 to 20	0 to 5
		CEM II/B-LL	65 to 79	–	–	–	–	–	–	–	–	21 to 35	0 to 5
	Portland-composite cement[c]	CEM II/A-M	80 to 94	<-- 6 to 20 -->									0 to 5
		CEM II/B-M	65 to 79	<--- 21 to 35 --->									0 to 5
CEM III	Blastfurnace cement	CEM III/A	35 to 64	36 to 65	–	–	–	–	–	–	–	–	0 to 5
		CEM III/B	20 to 34	66 to 80	–	–	–	–	–	–	–	–	0 to 5
		CEM III/C	5 to 19	81 to 95	–	–	–	–	–	–	–	–	0 to 5
CEM IV	Pozzolanic cement[c]	CEM IV/A	65 to 89	–	<--------------------- 11 to 35 --------------------->					–	–	–	0 to 5
		CEM IV/B	45 to 64	–	<--------------------- 36 to 55 --------------------->					–	–	–	0 to 5
CEM V	Composite cement[c]	CEM V/A	40 to 64	18 to 30	–	<----------- 18 to 30 ---------->			–	–	–	–	0 to 5
		CEM V/B	20 to 38	31 to 50	–	<----------- 31 to 50 ---------->			–	–	–	–	0 to 5

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[a] The values in the table refer to the sum of the main and minor additional constituents.

[b] The portion of silica fume is limited to 10%.

[c] In Portland-composite cements CEM II/A-M and CEM II/B-M, in Pozzolanic cements CEM IV/A and CEM IV/B and in composite cements CEM V/A and CEM V/B the main constituents other than clinker shall be declared by designation of the cement (for example see clause 8).

Fly ash and silica fume as hybrid admixture to Portland cement lowers the pH (Bach *et al.*, 2012), for example for cement with a composition of 37.5 wt% ordinary Portland cement, 32.5 wt% silica fume, fly ash.

Cements with the following hybrid mineral admixtures have improved physical and technical characteristics:

- silica fume + limestone (Antoni *et al.*, 2012);
- fly ash + limestone (De Weerdt *et al.*, 2011);
- granulated blast furnace slag + limestone (Hirao *et al.*, 2011);
- fly ash + limestone + diatomite (Gómez-Zamorano and Lozano-Vargas, 2011);
- metakaolin + carbon nanotubes (Morsy *et al.*, 2010);
- fly ash + carbon nanotubes (Chaipanich *et al.*, 2010);
- fly ash + nano calcium carbonate (Pera *et al.*, 1999).

The addition of 30% metakaolin and 15% limestone, for example, results in 100% increased strength characteristics of the cement at age 7–28 days. X-ray diffraction, differential thermal analysis and mercury porosimetry studies have shown that calcium carbonate reacts with aluminium metakaolin, forming additional aluminate phases and stabilizes the ettringite.

The addition of carbon nanotubes along with fly ash also increases the strength of cements.

3.2.5.2 Portland Cements with Organic-Mineral Admixtures

Most mineral admixtures lead to higher water requirement and reduce the workability of cement pastes. In this regard, it is reasonable to use mineral admixtures along with plasticizers as organic-mineral admixtures, which can reduce water requirement and improve the plasticity of the cement paste, providing a significant increase in their strength, density, impermeability, and frost and corrosion resistance.

Studies of organic-mineral admixtures with a large variety of mineral powders in combination with 1% naphthalene formaldehyde superplasticizer showed the possibility of obtaining of cement-based paste CEM I with 22–24 mm flowability and with water/solid ratio of 0.16–0.26 (Bajenov *et al.*, 2006). The following mineral powders were used: sandstone, diabase, silicate bricks, aerated concrete, limestone, granite, silica fume and fly ash. It was found that mineral admixtures increase the effectiveness of plasticizers, while the latter have a positive effect on the structure and properties of cements. The addition of 10% carbonate slurry of chemically treated water at power plants with 0.5% naphthalene formaldehyde superplasticizer caused an increase of cement strength of up to 80% (Tarakanov and Tarakanova, 2009).

The Institute of Concrete and Reinforced Concrete (Russian Federation) has developed organo-mineral modifiers of MC type (Kaprielov and Sheynfeld, 1997):

- MC-1, containing naphthalene formaldehyde superplasticizer, silica fume and hardening modifying agent – organophosphorus complexion;
- MC-C containing naphthalene formaldehyde superplasticizer, silica fume and fly ash which replaces 30–50% silica fume.

Organic-mineral modifiers of MC type are produced and used as a powdery product with an apparent density of 750–800 kg/m^3 and with grain sizes up to 100 μm.

The use of these admixtures provides an increase of storability of concrete consistency and the ability to increase the strength of the mixed binder up to 60–120%. This makes it possible to achieve concrete strength above 100 MPa.

Although immobilization of radioactive wastes does not require such high strength the addition of organic-mineral admixtures enables higher waste loadings to be achieved.

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4

Alternative Binders

Alternative or non-traditional cements form a large group of binders, significantly differing from Portland cement and from each other by the composition and type of the raw materials, the nature of hardening products, the mechanism of hardened cement paste formation, research experience, adoption and application.

Most alternative cements are special cements developed as a result of searching for ways to eliminate some of the disadvantages of Portland cement and/or development of special binders for special applications other than building. Some types of alternative binders, including special, also termed twenty-first century cements (Shi *et al.*, 2011), new cementitious matrixes (Palomo *et al.*, 2011), combining higher, in comparison with Portland cement, ‘ecological compatibility’ and some technical characteristics are becoming more and more promising in terms of partial replacement of ordinary Portland cement (OPC) in the present climate of ‘sustainable development’.

Many studies have stated the effectiveness of alternative binders for immobilization of toxic and radioactive wastes. Alternative cements have diverse composition of reaction products which compared with OPC are characterized by lower solubility and ion exchange properties, different pH, faster hardening, lower permeability of hardened pastes and so on. Alternative binders ‘push the envelope’ of cementation technology of toxic and radioactive wastes through:

- exhibiting in some cases higher efficiency on both physical isolation and chemical binding of heavy metals and radionuclides;
- widening the acceptance of wastes that can be immobilized by cementation;
- optimizing waste cementation technology in cases of problematic components of waste, providing faster curing of cementitious wasteforms and eliminating the need for pretreatment of waste, and so on;
- providing the possibility of using alternative binders as adsorbents and chemical additives.

Cementitious Materials for Nuclear Waste Immobilization, First Edition. Rehab O. Abdel Rahman,
Ravil Z. Rakhimov, Nailia R. Rakhimova and Michael I. Ojovan.

However, there are common current problems of improvement of cements for both building purposes and immobilization of toxic and radioactive wastes, including the improvement of their technological performance, corrosion resistance and durability of materials based on them. Development of blended and modified alternative binders via control of their composition and structure is a promising trend. Study of binding mechanisms of toxic and radioactive waste components results in data useful for prediction of their retention for a long time, durability of alternative cement-based matrices, and technological adoption. This chapter considers the most effective alternative binders for immobilization of toxic and radioactive wastes: calcium aluminate cements, calcium sulphoaluminate cements, phosphate cements and alkali-activated cements (AACs).

4.1 Calcium Aluminate Cements

The patenting (1908, Jules Bied) and the beginning of industrial application of calcium aluminate cement (CAC) (1913, Pavin de Lafarge) date from the early twentieth century. CAC belongs to special cements and is a fast-setting and high-strength hydraulic cement, the main characteristics of which are dominated by its low-basic calcium aluminates composition. The main raw materials for CAC production are limestone and bauxite. The use of bauxite means CAC is more expensive than OPC. Technological alumina and high-alumina slags obtained on smelting of ferroalloys are also used as raw materials for the production of high-alumina cements. There are two ways to produce CACs: either by applying sintering at about 1300°C which provides clinker formation due to reactions in the solid phase; or through complete melting of the whole mixture of raw materials at above 1400°C. CACs are characterized by lower CO_2 emission than OPC due to lower process temperature.

4.1.1 Chemical and Mineralogical Composition of CACs

Unlike Portland cement, which contains mainly lime and silica, CAC contains in addition to oxides of calcium and aluminium small amounts of oxides of iron, titanium and magnesium. The chemical composition of CAC is characterized by wider fluctuations than OPC and is determined by the method of clinker production and the quality of the raw materials used. Aluminium oxide is the main oxide (36–85%), providing calcium aluminate formation. Increase of its content increases refractoriness of CACs. Calcium oxide content is 16–42% and determines the mineralogical composition of CAC along with aluminium oxide. Reducing the CaO content below 16% reduces the strength of CACs. The presence of iron oxide is undesirable, so its content is limited to 0.2–2% depending on the type of CAC. Silica content above 10% is not desirable, its negative impact is due to the formation of non-hydratable gehlenite, $2SaO{\cdot}Al_2O_3{\cdot}SiO_2$. CACs are also characterized by the Al_2O_3/SiO_2 ratio, for example when this ratio equals 2 the CAC quality is low.

The main mineral of CAC is monocalcium aluminate (CA), $CaO{\cdot}Al_2O_3$, which after mixing with water and hardening, forms a high-strength paste and is responsible for its high strength and rapid hardening. Its structure is composed of AlO_4 tetrahedra and calcium atoms irregularly coordinated with six or seven oxygen atoms. Two atoms of calcium (Ca_2 and Ca_3) are surrounded by six oxygen atoms arranged octahedrally with Ca-O distances from 0.231 to 0.271 nm. The third calcium atom (Ca_1) is surrounded by nine oxygen atoms. A structural feature of CA is that Ca_1 is located at the end of an elongated octahedron and has bond lengths with oxygen from 0.24 to 0.29 nm. Irregular coordination of calcium atoms is responsible for the high hydration activity of CAC (Kouznetsova *et al.*, 1997).

Small quantities of $CaO{\cdot}2Al_2O_3{\cdot}(CA_2)$ and $12CaO{\cdot}7Al_2O_3{\cdot}(C_{12}A_7$, which in the literature is often given as $5CaO{\cdot}3Al_2O_3$) can be present in CACs. $C_{12}A_7$ mixed with water sets and hardens quickly. At first $C_{12}A_7$ demonstrates high strength, however with time the strength decreases. Conventional cements containing 20–30% CA_2 are characterized by finally high but slowly growing strength (Volgensky, 1979).

4.1.2 Hardening of CACs

Hardening of CAC is a result of interaction with water of its constituent minerals, primarily of its main component (CA) to form crystalline and amorphous hydrated reaction products. At limited water and temperature not higher than 20–22°C the reaction is as follows:

$$CaO{\cdot}Al_2O_3 + 10H_2O = CaO{\cdot}Al_2O_3{\cdot}10H_2O.$$

At a temperature of 22–30°C in the presence of water, CA gradually turns into dicalcium aluminate hydrate, $2CaO{\cdot}Al_2O_3{\cdot}8H_2O$, in the form of lamellar crystals of a hexagonal system. Simultaneously a gel-like aluminium hydroxide having sorptive properties is formed.

A feature of CAC is the ability of CAH_{10} and C_2AH_8 at temperatures above 30°C to convert into tricalcium aluminate hydrate, $3CaO{\cdot}Al_2O_3{\cdot}6H_2O$, following the change of the crystal habit and the release of hydrated alumina (gibbsite) and water. The reaction rate largely depends not only on temperature but also on the pH of the medium: the higher temperature and pH the more intense reactions of hexagonal low-basic aluminate hydrates transition to stable cubic C_3AH_6. Whilst conversion of metastable CAH_{10} and C_2AH_8 to a stable C_3AH_6 at ambient temperature (15–20°C) can last decades, it is completed in 3 days at 38°C, and within a few days or even hours at 50–60°C (Fryda *et al.*, 2008; Berger and Fryda, 2011).

Calcium aluminate $C_{12}A_7$ reacts with water to form the same hydrates as CA (C_2AH_8, CAH_{10} and C_3AH_6 with gibbsite). CA_2 and β-C_2S, interacting with water, form the corresponding hydrates.

The formation of calcium aluminate hydrates and CAC hardening occurs so rapidly that usually the cement paste has approximately 75–90% of the ultimate strength within 24 h from the time of mixing with water, and the strength development is completed in 3 days. It is worth considering in the hardening of CAC the negative effect on strength of temperatures above 25–30°C. The above described transition of hexagonal C_2AH_8 into cubic C_3AH_6 is accompanied by the appearance of stresses in the hardening cement paste and by a significant reduction of its strength. This should be taken into account when using CAC in addition to the fact that the hardening is accompanied by an intense heat evolution, reaching 70–80% of the total heat evolution in 24 h. This leads to the heating up of CAC-based materials to temperatures up to 25–30°C and above, with negative consequences for their strength.

For a better understanding of the reasons for CAC strength decreaseat temperatures above 30°C it is necessary to consider, that in the initial hydration stage 1 part by weight of CAC binds to 1.14 parts of water with the formation of CAH_{10}. Thus the absolute solid phase volume in the mix of CAC with water increases 3.7 times which promotes formation of a low-porosity hardened paste.

The transition of CAH_{10} into hardened C_3AH_6 following the scheme

$$3\left(CaO{\cdot}Al_2O_3{\cdot}10H_2O\right) = 3CaO{\cdot}Al_2O_3{\cdot}6H_2O + 2\left(Al_2O_3{\cdot}3H_2O\right) + 18H_2O$$

is accompanied by water release from the solid phase. The volume of the solid phase is reduced by 52.6% and paste porosity is abruptly increased with negative consequences for strength, air permeability and water permeability (Volgensky, 1979).

Solving the strength reduction ‘problem’ caused by the conversion of CAC hydrates is the subject of many studies (Ding *et al.*, 1995; Fryda *et al.*, 2008; Berger and Fryda, 2011). One way (Kouznetsova *et al.*, 1997) is the formulation of a binder that provides the optimum ratio of crystalline and gel phases after hydration. It allows production of hardened structures with high and stable strength. In the case when there is a gel-like phase between crystals, the rapprochement of crystals on their growth does not cause strength decrease, moreover in this case the structure densifies and paste strength increases. The gel-like phases play the role of ‘shock absorbers’ and of a bond (‘hinges’), providing the connection of crystals in a uniform skeleton without rigid fastening of elements of structure and reducing thus the pressure arising in the hardening structure.

Other ways to decreaselosses of strength of hardened CAC is by introduction of mineral admixtures such as granulated blast furnace slag and silica fume (Majumdar *et al.*, 1990; Ding *et al.*, 1995; Berger and Fryda, 2011; Kırca *et al.*, 2013). Their inclusion allows the prevention of transformation reactions of hydrates by the formation of stable phases (stratlingite and siliceous hydrogarnet). Gosselin (2009) found that introduction of granulated blast furnace slag and silica fume creates more space and increases the quantity of water for hydration of CAC; therefore more favourable conditions for CAC hardening are created.

4.1.3 Properties of CACs

The strength of CAC depends on temperature and also on its mineralogical composition and fineness. CAC with CA composition has relatively high early strength without an essential gain over a long time. CA_2 has low strength initially and reaches high strength over a long time of hardening. Regulating the CA/CA_2 ratio and the dispersity of cement, it is possible to obtain cements with uniform rate of strength development increase at all stages of hardening.

High fineness (above 320 m^2/kg) of CAC is unreasonable since the hydration of particles with sizes less than 40 μm causes a drop in strength between 3 and 28 days of hardening which results in no increase in the strength of polydisperse CACs. The fine grinding of CA_2 is helpful as the strength of cement is increased in accordance with increase of fineness.

CAC is characterized by high heat, chemical and freeze–thaw resistance. Improved sulphate resistance, resistance to mineralized waters and some acids of CACs are explained by the aluminium hydroxide, formed on hydration, which envelops particles of cement and calcium aluminate hydrates, protecting them from the corrosive environment. At the same time, CACs are unstable in solutions of alkalis and ammonium salts. Hardened CAC cement paste is more cold-resistant than OPC, which to a great extent is caused by the enhanced density of hardened cement paste. The porosity of hardened CAC paste is approximately

1.5 times less than that of OPC. This also explains the higher water resistance of CACs. Lower CAC hardened paste porosity is the result of high hydration degree, higher water involvement in hydration and also by the formation of a significant amount of gel-like aluminium hydroxide (Volgensky, 1979; Kouznetsova *et al.*, 1997).

Fast hardening, high strength, low permeability, high freeze–thaw and corrosion resistance of hardened CAC paste, the sorptive ability of $Al(OH)_3$ and ion-exchange ability of ettringite (formed on introduction of lime, calcium sulphate) (Amathieu and Estienne, 2003) in a complex are the properties that make CACs efficient as matrixes for immobilization of wastes. To the properties listed it is necessary to add the efficiency of CAC with respect to compatibility with components of the waste impeding setting and hardening of OPC. The feasibility of effective waste immobilization using CAC and blended CAC for waste containing Cr, Cd, Pb, Zn, Mg, Sn, Cs, liquid borates, radioiodine, and so on has been demonstrated (Fryda *et al.*, 1996; Goni and Guerrero, 2001; Madrid *et al.*, 2001; Toyohara *et al.*, 2002; Nithya *et al.*, 2009).

CACs are used in France for (non-radioacti ve) hazardous waste encapsulation as a substitute for OPCbased cements in order to improve setting and leaching behaviour (Berger and Fryda, 2011).

Chemical binding of hazardous and radioactive contaminants by CACs can be improved by the introduction of various admixtures with hydration products with ion-exchange properties being formed. It is feasible to include in cement matrices up to 50% of calcium sulphate in the form of gypsum or anhydrite (Amathieu and Estienne, 2003) or 5–10% slaked or not slaked lime, and limestone for formation of hydration products of calcium sulphoaluminate composition, siliceous mineral admixtures for formation of zeolitic phases (Fryda *et al.*, 1996). The technological and physico-mechanical properties of CACs simultaneously improve.

CACs and mixed CACs are also suitable as chemical additives (chemical reactants) for clearing solutions with low contaminant content, and in more concentrated solutions for decreasing undesirable interactions between components of waste with cements (Berger and Fryda, 2011).

4.2 Calcium Sulphoaluminate Cements

Whatever the merits of OPC one of its drawbacks is the shrinkage of materials based on it. As shown in Chapter 2 for OPC and its variants and in Section 4.1 for CACs on their hydration crystalline and colloidal hydrates are formed. Colloidal hydrates on hardening in air dry and compact with time which causes shrinkage of cement paste. Shrinkage depends on the type of cement used, its fineness, water/cement ratio, granulometric composition of fillers and curing conditions. It is not possible to avoid shrinkage via optimizing and combining these factors. Attempts to create a cement without shrinkage have led to the creation of calcium sulphoaluminate cements (CSACs). These special cements can be shrinkage compensating, expansive and self-stressing for various uses. The creation and manufacture of CSACs took place in the 1960–1970s. Now they are made in industrial volumes, and since 2004 world production has been 1.2–1.3 million t per year (Wang, 2010).

The basis of CSAC is calcium sulphoaluminate clinker which is a product of burning at 1200–1300°C a raw mix consisting of lime, an aluminous component and gypsum, calculated to form calcium sulphoaluminate, calcium aluminates $C_{12}A_7$ or CA and also C_2S and C_4S. Unlike Portland cement clinker, the mineral formation of which comes to an end in the clinker melt, production of calcium sulphoaluminate clinker is characterized by solid phase reactions without melt participation. The advantages of calcium sulphoaluminate clinker over Portland cement clinker are lowered CO_2 emission and grinding expenses. The basic raw materials for manufacture of calcium sulphoaluminate clinker are:

- calcium-containing rocks – limestone, chalk;
- sulphate-containing components – gypsum, phosphogypsum, fluorine-anhydrite;
- alumina-containing natural rocks – bauxite, kaolin, alunite, high-alumina clay and also wastes of the petrochemical and chemical industry, high-alumina wastes of ferrous and nonferrous metallurgy.

Essential and 'useful' oxides in raw materials on manufacture of calcium sulphoaluminate clinker are CaO and Al_2O_3, admixtures – SiO_2, Fe_2O_3, MgO, R_2O, P_2O_5 and others. The main attention for the estimation of the chemical composition of raw materials is given to the SiO_2 and Fe_2O_3 content as these oxides interfere with the formation of calcium sulphoaluminate during its synthesis connecting CaO and Al_2O_3 into low hydraulic activity C_2AS and C_4AF compounds.

4.2.1 Chemical and Mineralogical Composition of CSACs

The chemical composition of calcium sulphoaluminate clinker in terms of oxide is as follows (wt%): Al_2O_3, 8–47%; CaO, 36–61%; SiO_2, 3–27%; Fe_2O_3, 1–13%; SO_3, 3–15% (Cau-dit-Coumes, 2013). The main mineral in CSAC at a content of 30–70 % is tetracalcium trialuminate sulphate, $C_4A_3\,\overline{S}$ (ye'elimite, also called Klein's compound) (Klein, 1963), which is formed by burning of the raw mix in the reaction (Havlica and Sahu, 1992; Sharp *et al.*, 1999; Juenger *et al.*, 2011):

$$3CaCO_3 + 3Al_2O_3 + CaSO_4{\cdot}2H_2O \rightarrow 4CaO{\cdot}Al_2O_3{\cdot}SO_3 + 3CO_2 + 2H_2O.$$

Its crystalline structure consists of a three-dimensional framework of AlO_4 tetrahedra sharing corners, with Ca^{2+} and SO_4^{2-} ions located in the existing cavities. It belongs to the tetragonal system. Above about 1350°C this phase becomes unstable and starts to decompose. The Al^{3+} within the structure of the C_4A_3S phase may be partially substituted by Fe^{3+} ions. The reactivity of this phase will decline with iron content in the crystalline lattice (Odler, 2000).

The second most important mineral in sulphoaluminate–belite cements is belite, C_2S – $CaO{\cdot}SiO_2$ (Odler, 2000; Juenger *et al.*, 2011).

4.2.2 Hardening of CSACs

Calcium sulphoaluminate clinker is ground simultaneously with 25% gypsum for the purpose of regulating setting, strength and its development, and soundness. Introduction of other admixtures such as OPC and limestone is also possible and effective (Paglia *et al.*, 2001; Marchi and Costa, 2011). The structure of the hydration products and final properties of CSAC depend on the presence and content of gypsum and other admixtures. Figure 4.1 shows the phase development of CSACs as a function of time (Winnefeld and Lothenbach,

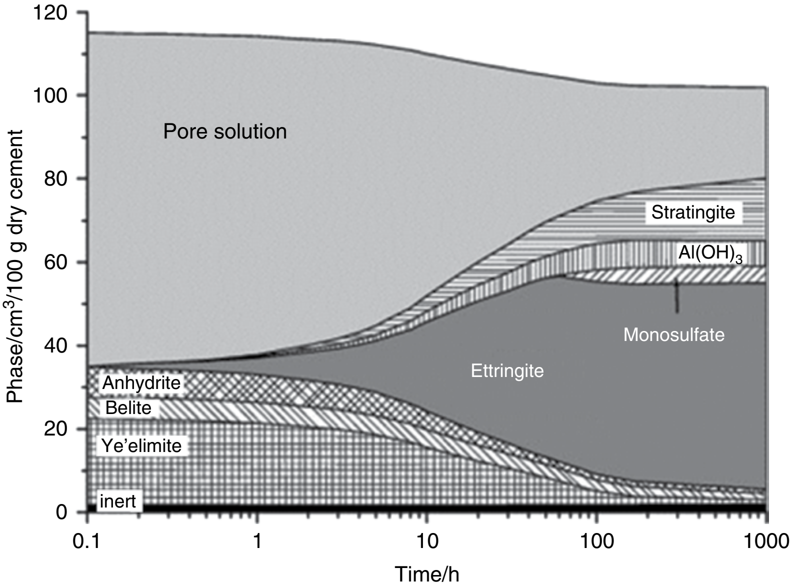

Figure 4.1 *Phase development of a CSAC (water/cement = 0.80) as a function of hydration time calculated by thermodynamic modelling Reproduced with permission from Winnefeld and Lothenbach, 2010 © 2010, Elsevier*

2010). On interaction of calcium sulphoaluminate with water, calcium monosulphoaluminate hydrate (AFm) and aluminium hydroxide are formed:

$$C_4A_3\overline{S} + 18H \rightarrow C_3A \cdot C\overline{S} \cdot 12H + 2AH_3.$$

TheAFm phase belongs to the lamellar double hydroxide large family. Its crystal structure is composed of positively charged main layers $[Ca_2Al(OH)_6]^+$ and negatively charged interlayers $[1/2SO_4 \cdot nH_2O]^-$ (Albino *et al.*, 1996).

With gypsum the interaction of $C_4A_3\overline{S}$ with water is accelerated and in addition to amorphous aluminium hydroxide ettringite is formed, $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$ or $C_3A \cdot 3C\overline{S} \cdot 32H$ in a molar ratio of $C_4A_3\overline{S}$ to $C\overline{S}$ not less than 1:2 via the reaction:

$$C_4A_3\overline{S} + 2C\overline{S}H_2 + 34H \rightarrow C_3A \cdot 3C\overline{S} \cdot 32H + 2AH_3,$$

or a mixture of ettringite, $C_3A \cdot 3C\overline{S} \cdot 32H$ and $C_3A \cdot C\overline{S} \cdot 12H$ is formed on total consumption of gypsum in reaction (Juenger *et al.*, 2011).

Ettringite is composed of positively charged columns $[Ca_3Al(OH)_6]^{3+}$ and of negatively charged channels $[3/2SO_4 \cdot nH_2O]^{3-}$. The structural flexibility of calcium monosulphoaluminate hydrate and ettringite in the sense of ion exchange gives CSACs the ability to chemically bind many elements of both anionic and cationic nature (Peysson *et al.*, 2005; Zhou *et al.*, 2006; Cau-dit-Coumes *et al.*, 2009).

Intensive hydration of $C_4A_3\overline{S}$ and binding of free water provide fast consolidation of structure, short setting and an accelerated strength development. Ettringite formation is accompanied by volume increase of the solid phase which, depending on the volume, can cause expansion and pressure in hardening cement. The expansion is due to the volume increase of the solid phase and is connected to the part which is not accommodated in the pore space of the hydrating cement paste (Kouznetsova *et al.*, 1997).

Hydration of the belite component C_2S causes long strength development increase and facilitates the relaxation of pressure on the crystallization of ettringite.

Strätlingite (C_2ASH_8), C–S–H, CAH_{10} or siliceous hydrogarnet can be also formed depending on clinker composition, presence and type of admixtures (Cau-dit-Coumes, 2013).

The increase of gypsum content allows the production of various types of CSACs, namely CSACs that are rapidly hardening or high early strength cements with a molar ratio of gypsum (anhydrite) to $C_4A_3\overline{S}$ equal to 0–1.5; at a ratio equal to 1.5–2.5 CSACs are expanding, and at ratio equal to 2.5–6 they are self-stressing cements (Zhang, 2000).

Rapid-hardening and high-strength CSACs are of interest for immobilization of radioactive wastes (Cau-dit-Coumes, 2013).

4.2.3 Properties of CSACs

Hardened CSAC paste is characterized by (Shi *et al.*, 2011; Cau-dit-Coumes, 2013):

- short setting times – from 30 min to 4 h;
- higher early strength compared with Portland cement;
- low permeability due to the predominance of pore radius less than 25 nm;
- durability which is not inferior to that of Portland cement;
- high freeze–thaw resistance;
- chemical resistance to sea water, sulphates, and magnesium and ammonium salts;
- the pH of CSACs (pH 10.5–11); this makes them less than 100–300 times as alkaline as Portland cement (pH 13).

In addition CSACs compared with Portland cements are much more sensitive to temperature, water/cement ratio and introduction of pozzolanic admixtures.

The relatively high and non-uniform (in time) heat evolution is also a characteristic of CSACs. Especially rapid development of the process is characteristic for the initial period. The exothermic reactions and, consequently, the heat evolution start after 1 h and reach a maximum after 2 h from the moment of mixing. By 1 day 80% of the total heat is released; this value is 70% for CACs, and is 20% for Portland cement (Figure 4.2). It is possible to introduce into CSACs mineral admixtures for reducing undesirable heat evolution during waste cementation.

According to the results of numerous studies analysed in Cau-dit-Coumes (2013), and published in the Proceedings of NUWCEM 2011 (2011), the use of CSACs as a matrix for immobilization of toxic and radioactive wastes can:

- accommodate heavy metals (Cr, Pb, Zn, Cd, etc.) and ion exchange resins;
- enable immobilization of wastes which are problematic to Portland cement such as those containing aluminium and uranium and producing hydrogen through their interaction with cement, and radioactive sludge with a high content of sulphate and borate ions;

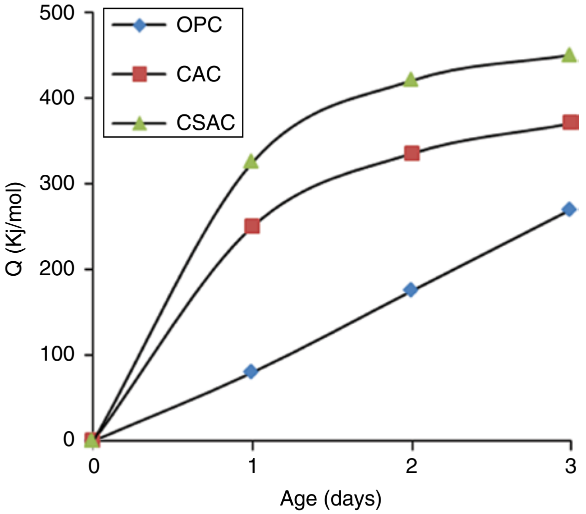

Figure 4.2 *Heat evolution of cements with time. OPC, ordinary Portland cement; CAC, calcium aluminate cement; CSAC, calcium sulphoaluminate cement(Kouznetsova et al., 1997). Reproduced with permission from T. Kouznetsova*

- shorten the waste cementation process due to the high rate of hydration and avoid pretreatment enabling solidification of wastes containing components which make setting and hardening of Portland cement-based compounds difficult, for example waste containing zinc and boron.

4.3 Phosphate Cements

The production of this group of binders is based on the synthesis of phosphate compounds using acid–base reactions of solids of basic nature (CuO, FeO, ZnO, CaO, MgO, etc.) and high reactive liquid activators comprising phosphate anions. Activators that can be used include aqueous phosphoric acid (mainly orthophosphoric acid, H_3PO_4) and acid phosphate salt solutions, for example solutions of KH_2PO_4, $NH_4H_2PO_4$ and $CaHPO_4$.

In addition to the fundamental differences in the mechanism of formation of hardened paste, phosphate binders have a wider chemical and structural composition compared with other types of binders which is proved by a number of fundamental chemical characteristics of phosphate compounds. Figure 4.3 shows the structure of phosphoric acid (Golynko-Volfson *et al.*, 1968).

Orthophosphoric acid is polybasic and has three stages of ionization, which provides multidimensional stereometric chemical binding and the possibility of forming numerous connection options of varying degrees of substitution (mono-, di- and trisubstituted salts). An important source of strength formation is also a structural characteristic of phosphoric acid and phosphates having a branched network of hydrogen bonds. Finally, orthophosphoric acid and its derivatives have a high predisposition to associate functional groups, to polycondensation and to complexation.

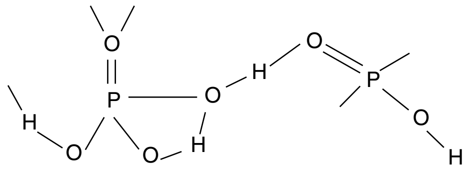

Figure 4.3 Structure of phosphoric acid (Golynko-Volfson et al., 1968)

Table 4.1 Conditions for exhibiting binding properties of oxide-orthophosphoric acid systems (Kouznetsova et al., 1997)

Oxide	Electron work function (eV)	Ionic potential of cation (z/r)	Conditions for exhibiting binding properties
SiO_2, TiO_2, Al_2O_3, ZrO_2, MnO_2, Cr_2O_3, Co_2O_3, SnO_2	More than 4.5	5.0	Intensification of acid–base interactions required
Fe_2O_3, Mn_2O_3, NiO, CoO, FeO, CuO	3.3–4.3	2.5–4.4	Hardening in normal conditions
Nd_2O_3, La_2O_3, MgO, ZnO, CdO	2.5–3.3	2.0–3.0	Passivation of acid–base interactions required
CaO, SrO, BaO, PbO	Less than 2.0	1.4–2.0	Emergency measures of passivation of acid–base interactions required

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The powder part of phosphate cements influences the cements depending on the binding properties ofthe 'oxide–phosphoric acid' systems and the ionic potential of the cations in the oxide. Conditions for exhibiting binding properties of oxide–orthophosphoric acid systems are listed in Table 4.1.

Acceleration of setting and hardening occurs on decreasing the ionic potential of the cation or electron work function and vice versa, with the increase of ionic potential this process slows down. With increase of oxide reactivity with respect to acid the transition, occurs from phosphate systems which harden only on heating or mechano-chemical activation to systems which harden in normal conditions, and further to systems which exhibit binding properties on increasing the intensity of activation. Therefore a necessary condition to exhibit binding properties is the adjustment of chemical interaction rates between components of phosphate cement systems with the rate of formation of structure. To decrease the intensity (rate) of reactions and to obtain normally hardening binders oxides are replaced by mono- and disubstituted phosphates. Normally hardening cements containing bivalent metals with phosphoric acid are also produced under this scheme. In cases when oxides are comparatively inert for hardening at room temperature, hydroxides are applied instead, and heating of cement paste is used approximately up to 300°C. Both natural and artificial mineral products with complex chemical–mineralogical composition can be used as starting solid components when intensities (rates) of basic chemical interaction and structure formation processes are adjusted. For example, combinations of micas, serpentinite, clay minerals, talc, volastonit and other minerals and rocks with phosphate solutions form phosphate binder systems with valuable properties (Golynko-Volfson *et al.*, 1968).

4.3.1 Properties of Phosphate Cements

Phosphate cements are special cements. Currently they are most widely used in dentistry and medicine. Table 4.2 compares the properties of phosphate cement and OPC (CCHRC, 2010).

Fast hardening, high adhesive strength to concrete and metals, and high bending and compressive strength are intrinsic characteristics for phosphate cements. The compressive strength can reach 150 MPa after 24 h. For example, magnesium-ammonium phosphate cement representing a mix of ammonium phosphate and magnesium oxide in 1 h after mixing with water demonstrates strength up to 14 MPa. The hardening basis is the synthesis of double magnesium-ammonium phosphate, $NH_4MgPO_4{\cdot}6H_2O$ and magnesium phosphate, $Mg_3(PO_4)_2{\cdot}4H_2O$. Volastonit-phosphate cement which is the combination of ground volastonit and partially neutralized orthophosphoric acid shows strength of up to 50 MPa after 4 h of hardening. Zinc-phosphate cement (the combination of a powder of modified zinc oxide and partially neutralized orthophosphoric acid) shows strength of up to 10 MPa after 24 h of hardening.

Besides strength, the characteristics of phosphate cements differ from OPC in terms of their high temperature and chemical resistance. On heating, all water-containing binder systems lose physical and constitutional water. This process always causes destruction of hydro-hardened binder systems, which leads to an essential (up to 90%) loss of the strength obtained on hardening. Thermal degradation of phosphate cements as a rule is combined with polycondensation and polymerization processes that favourably affect strength development. As a result, on increase in temperature to the dehydration temperature a decrease in strength of phosphate cements is not observed at all, or it is significantly smaller than in systems of hydration hardening. Phosphate cement systems can be used at high and very high temperatures. The properties of reaction products formed on hardening of phosphate cements in many cases allow these systems to be associated with materials with high chemical resistance (Kouznetsova *et al.*, 1997).

It is expedient to consider magnesium and calcium phosphate cements in detail.

Table 4.2 *Physical–mechanical properties of OPC and phosphate cements (special mix designs yield different results)*

Property	OPC	Phosphate cement
Compressive strength (MPa)	20–50	55–80
Bending tensile strength (MPa)	2–7	6–11
pH tolerance	6.5–14	3–11
Salt tolerant (continuous exposure)	No	Yes
Max. structural temperature (K)	1090	1530
Curing time (demolding)	1–2 days	10 min to 2 h
Curing time (high strength) (days)	28	3
Curing temperature range (K)	258–488	260–316
Bonds to itself	No	Yes
Bonds to reinforcement	No	Yes
Shrinks upon drying	Yes	No
Coefficient of thermal expansion (1/K)	0.000012	~0.00000017
Absorbs water	Yes	No
Foamable	Yes	Yes

4.3.2 Magnesium Phosphate Cements

The raw materials for magnesium phosphate cements are orthophosphoric acid or $(NH_4)_2HPO_4$ (diammonium hydrogen phosphate) and MgO which is a product of thermal treatment of magnesite. The main result of their interaction is struvite. $NH_4MgPO_4{\cdot}6H_2O$:

$$MgO + (NH_4)2HPO_4 + 5H_2O \rightarrow NH_4MgPO_4{\cdot}6H_2O + NH_3,$$

which determines the setting and hardening of this type of phosphate cement.

Properties of magnesium phosphate cements valuable for building purposes are fast hardening and good adhesion to concrete and metals that predetermines their usefulness for repair works (Yang *et al.*, 2000).

There is experience in development of magnesium phosphate cement to immobilize radioactive wastes. A magnesium phosphate binder termed ceramicrete has been developed at Argonne National Laboratory (USA) to immobilize problematic low-level mixed wastes. The starting materials of ceramicrete are MgO and monopotassium phosphate, KH_2PO_4, and after hardening it consists of $MgKPO_4{\cdot}6H_2O$ (Wagh *et al.*, 1997a). Ceramicrete has the following characteristics: a compressive strength of 20–30 MPa; density of approximately 1.8 g/cm^3; an open porosity of 2–5%; and pH 6–8 of the pore solution (Wagh *et al.*, 1997b). Good results were obtained on immobilization by this cement-based matrix of wastes containing ^{137}Cs (Singh *et al.*, 1998), ^{99}Tc (Mayberry *et al.*, 1992), Pu-containing combustion residues (Wagh *et al.*, 1999a) and highly saline effluents (Wagh *et al.*, 1999b).

The solidification of wastes with a high content of Cd, Cr, Cu, Ni, Pb and Zn by magnesium phosphate binders is also possible (Buj *et al.*, 2010). A magnesium phosphate binder has been designed for immobilization of spent nuclear fuel and liquid and solid radioactive wastes (Sharygin *et al.*, 2009).

4.3.3 Calcium Phosphate Cements

The bases of calcium phosphate cements are calcium phosphates of diverse composition or their blends with calcium salts (sulphate, carbonate, hydroxide, aluminate, calcium, etc.), magnesium orthophosphates, strontium and so on (Dorozhkin, 2009).

Diverse combinations of calcium and phosphorus oxides (in the presence or absence of water) give a sufficiently large variety of different calcium phosphates so there is wide range of raw materials for calcium phosphate cement production.

Solubility in water, binding properties and calcium phosphate cement pHs are substantially determined by the Ca/P ratio. Table 4.3 lists some of the characteristics and types of calcium phosphate cements (Dorozhkin, 2007).

Hardened calcium phosphate cement consists of stoichiometric hydroxyapatite (HA) or calcium-deficient hydroxyapatite. Their formation results from two types of reactions. A classical example of the first type of reaction is based on acid–base interaction, for example the reaction of basic tetracalcium phosphate and acidic dicalcium phosphate anhydrous in an aqueous medium with the formation of poorly crystallized HA (Brown and Chow, 1985):

$$2Ca_4(PO_4)_2O + 2CaHPO_4 \rightarrow Ca_{10}(PO_4)_6(OH)_2.$$

Table 4.3 Existing calcium orthophosphates and their major properties (Dorozhkin, 2007)

Ca/P ionic ratio	Compound and its abbreviation	Chemical formula	Solubility at 25°C, $-\log(K_s)$	Solubility at 25°C, (g/l)	Stability at aqueous solution at 25°C (pH range)
0.5	Monocalcium phosphate monohydrate (MCPM)	$Ca(H_2PO_4)\cdot H_2O$	1.14	~18	0.0–2.0
0.5	Monocalcium phosphate anhydrous (MCPA)	$Ca(H_2PO_4)_2$	1.14	~17	[a]
1.0	Dicalcium phosphate dihydrate (DCPD), mineral brushite	$CaHPO_4\cdot 2H_2O$	6.59	~0.088	2.0–6.0
1.0	Dicalcium phosphate anhydrous (DCPA), mineral monetite	$CaHPO_4$	6.90	~0.048	[a]
1.33	Octacalcium phosphate (OCP)	$Ca_8(H_2PO_4)_2(PO_4)_4\cdot 5H_2O$	96.6	~0.0081	5.5–7.0
1.5	α-Tricalcium phosphate (α-TCP)	$\alpha\text{-}Ca_3(PO_4)_2$	25.5	~0.0025	[b]
1.5	β-Tricalcium phosphate (β-TCP)	$\beta\text{-}Ca_3(PO_4)_2$	28.9	~0.0005	[b]
1.2–2.2	Amorphous calcium phosphate (ACP)	$Ca_xH_y(PO_4)_z\cdot nH_2O$, $n = 3–4.5$	[c]	[c]	~5–12[d]
1.5–1.67	Calcium-deficient hydroxyapatite (CDHA)[e]	$Ca_{10-x}(HPO_4)_x(PO_4)_{6-x}(OH)_{2-x}$[f]	~85.1	~0.0094	6.5–9.5
1.67	Hydroxyapatite (HA)	$(0 < x < 1)$			
1.67	Fluoroapatite (FA)	$Ca_{10}(PO_4)_6(OH)_2$	116.8	~0.0003	9.5–12
2.0	Tetracalcium phosphate	$Ca_{10}(PO_4)_6\,F_2$	120.0	~0.0002	7–12
	(TTCP), mineral hilgenstockite	$Ca_{10}(PO_4)_2O$	38–44	~0.0007	[b]

[a] Stable at temperatures above 100 °C.

[b] These compounds cannot be precipitated from aqueous solutions.

[c] Cannot be measured precisely. However, the following values were found: 25.7 ± 0.1 (pH = 7.40), 29.9 ± 0.1 (pH = 6.00), 32.7 ± 0.1 (pH = 5.28).

[d] Always metastable.

[e] Occasionally CDHA is named as precipitated HA.

[f] In the case $x = 1$ (the boundary condition with Ca/P = 1.5), the chemical formula of CDHA is as follows: $Ca_9(HPO_4)(PO_4)_5(OH)$.

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The second type of reaction is the hydrolysis of metastable orthophosphate in an aqueous medium (Dorozhkin, 2009).

The calcium phosphate cements are widely used in medicine and dentistry because HA has a high affinity for human bone tissue. In addition, the HA structure resembles the structure of zeolites characterized by thepresence of channels of diameter 2.5Å and 3–4.5Å (Kay *et al.*, 1964).

HA shows structural flexibility in ion exchange with contaminant ions, often containing trivalent lanthanides and actinides, replaced by calcium (Glasser, 2011). This property of HA combined with low solubility, three to four times less than that of calcium silicate hydrate and portlandite (Cau-dit-Coumes, 2013), makes phosphate cements effective and promising for the immobilization of toxic and radioactive waste.

4.4 Alkali-Activated Cements

Production of AACs is based on alkaline (hydroxides, carbonates, silicates, alkali metal sulphates) activation of fine aluminosilicate materials of natural origin and of waste products.

Using the composition of cementitious component(s) as a criterion, AACs can be classified into five categories (Shi *et al.*, 2006, 2010):

- alkali-activated slag-based cements;
- alkali-activated pozzolan cements;
- alkali-activated lime-pozzolan/slag cements;
- alkali-activated calcium aluminate blended cements;
- alkali-activated Portland blended cements (hybrid cements).

The most used AACs in research, development and practical implementation including immobilization of radioactive wastes are alkali-activated granulated blast-furnace slag, fly ash of industrial waste and thermally activated clay minerals (metakaolin).

The AAC structure formation mechanism is significantly different from conventional hydraulic cements hardening. According to the theory of hydration and hardening of alkaline binders and dispersed structures (Rebinder, 1968; Glukhovsky, 1979), AAC structure formation is represented by a combination of physical and chemical transformations occurring in series and parallel, among which the main ones are:

- destruction of the starting dispersed phase to a unstable structure of certain units (hydrated $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedra Ca^{2+}, $Ca(OH)^+$, $Ca(H_2O)OH^-$ ions, etc.);
- their interaction with the formation of thixotropic disperse-coagulation units;
- development on the base of their condensation–crystallization structure of hydrate reaction products.

The properties of AACs depend on more factors than that of OPC due to the fact that in addition to the chemical and mineralogical composition of the binder and fineness, the hardening and properties also depend on the nature and concentration of the alkali activator. Influence of the aluminosilicate component is predetermined mainly by the presence and quantitative content of the amorphous phase and calcium content in its composition.

Figure 4.4 shows the $CaO–Al_2O_3–SiO_2$ ternary diagram of cementitious materials.

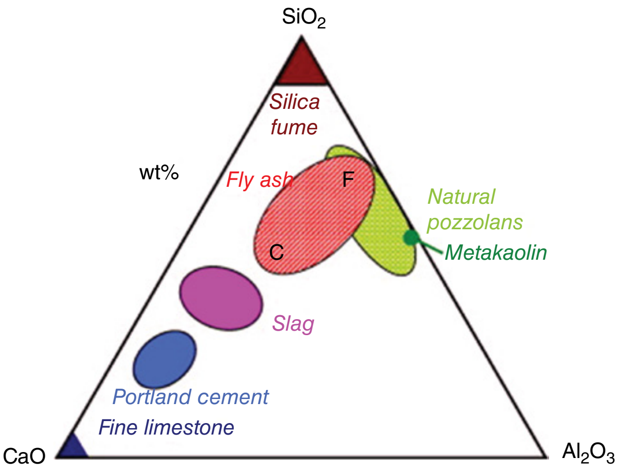

Figure 4.4 CaO–Al_2O_3–SiO_2 ternary diagram of cementitious materials. Reproduced with permission from Lothenbach et al., 2011. © 2011, Elsevier

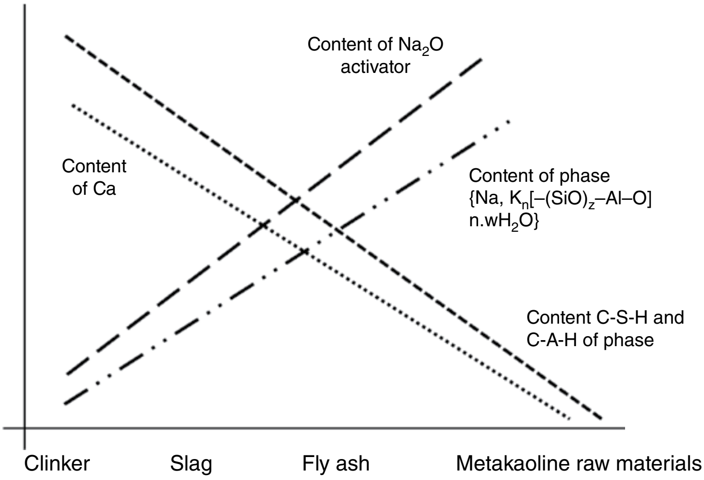

Figure 4.5 Composition of various alkali activated materials. Reproduced with permission from Skvara, 2007

Granulated blast furnace slag and class C fly-ash belong to calcium aluminosilicates and class F fly-ash belongs to low- or non-calcium aluminosilicates. The chemical composition analysis of granulated blast furnace slags of nine countries, presented in Shi *et al.* (2006), revealed the content of the main oxides: CaO, 34.7–42.9%; MgO, 6.1–14.6%; Al_2O_3, 9–13.9%. Fly ashes according to ASTM C 618 (2003) are divided into two classes: C [70% > (SiO_2 + Al_2O_3 + Fe_2O_3) > 50%] and F [(SiO_2 + Al_2O_3 + Fe_2O_3) > 70%]. The chemical composition of metakaolin ($Al_2Si_2O_7$) is: SiO_2, 49–52%: Al_2O_3, 40–43% (Li *et al.*, 2010).

With a decrease in the calcium content in the binder the required alkali content increases (K_2O, Na_2O, Li_2O) (Figure 4.5), which for an alkali-activated slag-cement

(AASC) is 2–8%, for AACs based on ash is 5–10% and for AACs based on metakaolin is 10–20% (Krivenko and Kavalerova, 2008). The calcium contents also varies the nature of the binder gel and final properties of binders. Final properties, namely strength, permeability and other characteristics, essentially depend on the specific surface of the AAC aluminosilicate component, nature of the alkaline component and the hardening process. Best results are achieved when alkali aqueous solutions of silicates and alkali metal aluminates containing low-polymeric ions with binding properties are used as activators.

AACs can be classified into two groups based on duration of study and application: AASCs and geopolymers**.**

Extensive research of AACs began in the late 1950s with AASCs based on the alkaline-earth alkali binding system $Me_2O–MO–Al_2O_3–SiO_2–H_2O$ using granulated blast furnace slag. Alkaline activation of ground granulated blast furnace slag allowed production of hydraulic binders without burning and Portland clinker use. The main reaction products are low-basic calcium silicate hydrates, although hydrogarnets and sodium aluminate hydrates can be also present (Glukhovsky, 1979).

Formation of calcium silicate hydrate in the system of ground granulated blast furnace slag and sodium silicate solution occurs as follows: Corrosion of slag glass occurs as a result of the ionic exchange $2Na^+ \leftrightarrow Ca^{2+}$ under the influence of Na^+ liberated from sodium silicate activator. This leads to breaking of bonds –Si–O–Si – in the slag glass and to hydration of surface layers of its particles with formation on them of shells made of silicic acid – sodium silicate gel. When the solution is enriched by Ca^{2+}, Mg^{2+} then $Ca(OH)_2$, $Mg(OH)_2$ and $Ca(CO)_3$ crystallize. Gel-like shells formed on slag particles adsorb Ca^{2+} ions from the solution and gradually convert into low-basic calcium silicate hydrates with release of NaOH into solution. Liberated NaOH interacts again with slag, destroying its structure. Simultaneously with the described process the following reaction occurs:

$$n\mathrm{Na_2O}\cdot m\mathrm{SiO_2}\cdot p\mathrm{H_2O} + x\mathrm{Ca}^{2+} + \mathrm{aq}\cdot + y\mathrm{OH}^{-}\mathrm{aq}\cdot \rightarrow x\mathrm{CaO}\cdot\mathrm{SiO_2}\cdot\mathrm{H_2O} + \mathrm{NaOH},$$

leading to precipitation of calcium silicate hydrates from solution (Volgensky, 1979).

Low basic calcium-silicate gel derived from the alkali activation of blast furnace slag is hardly crystallized with a moderate degree of aluminium substitution and a low C/S ratio and therefore is denoted as C–(A)–S–H gel (Richardson *et al.*, 1994; Wang and Scrivener, 1995; Lecomte *et al.*, 2006; Garcia-Lodeiro *et al.*, 2011; Puertas *et al.*, 2011).

The production technology of AASC-based materials is similar to that of OPC, except for the preparation of alkali activator solution when it is introduced as a solution; moreover the curing time and temperature can be reduced in comparison with OPC in case of the need to improve the strength development.

The hardened AASC favourably differs from OPC (Glukhovsky, 1979; Shi *et al.*, 2006, 2011) by:

- higher strength of certain compositions;
- less porosity and pore sizes (<100Å);
- high corrosion resistance to most types of aggressive media;
- heat resistance.

The maximum strength and best structural characteristics are achieved by grinding the slag to fineness of 600 m^2/kg at granulometric distribution close to that optimal for OPC: <5 μm, 22%; 5–10 μm, 15%; 10–20 μm, 24%; 20–50 μm, 29%; >50 μm, 10%; or <3 μm, 15%; 3–30 μm, 61%; 30–60 μm, 16%; >60 μm – 8%, and using sodium silicate as activator (Glukhovsky, 1979; Shi *et al.*, 2006; Rakhimova and Rakhimov, 2012a).

There are applications (1986–1994) and numerous results of research of durability of AASC concretes summarized in Shi *et al.* (2006). Now blast furnace slag is a valuable raw material, the cost of which being near to that of OPC. In addition, both blast furnace slags and ashes are available in much smaller quantities than Portland cement and are not available everywhere (Scrivener and Nonat, 2011). Therefore alkali-activated slag blended cements are perspective containing up to 80% of various mineral admixtures. It is expedient to replace the slag by ground materials such as ashes, red clay brick waste, quartz sand, natural and synthetic zeolites, concrete and demolition waste, and silica fume (Puertas and Fernandez-Jimenez, 2003; Rakhimova, 2008; Bilek, 2011; Rakhimov and Rakhimova, 2011; Rakhimova and Rakhimov, 2011, 2012a, b; Rakhimova *et al.*, 2012; Rashad, 2013). The use of even a small amount of blast furnace slag as part of blended AASC in combination with alkaline activation gives positive results on combination of slag with mineral admixtures not effective or having low efficiency for the production of blended OPC.

The technical advantages of AASCs listed above are caused among other factors by the low basicity of C–(A)–S–H, absence of portlandite and ettringite in the reaction products of hardened AASC. Curing temperature increase up to 300°C promotes the formation of well crystallized low-basic calcium silicate hydrate, tobermorite and xonotlite, characterized by an enhanced ion exchange ability and retention of contaminants (Komarneni and Roy, 1985; Shrivastava and Glasser, 1985; Komarneni *et al.*, 1986, 1988; Shi *et al.*, 1991; Sugama and Brothers, 2004; Shi and Fernandez-Jimenez, 2006). Low basicity of reaction products in a complex with low porosity of hardened state gives the high efficiency of AASC as a matrix for immobilization of radioactive wastes.

A detailed analysis of studies on AASCs for immobilization of radioactive wastes is presented in the monograph by Shi and Fernández-Jiménez (2006). Solidification of wastes containing heavy metals (Zn^{2+}, Pb^{2+}, Cd^{2+} and Cr^{6+}, Hg^{2+}, etc.) and radionuclides (Cs^{+}, Sr^{2+}) is effective by using AASCs. Radioactive metals (Na, K, Cs), used sodium–potassium coolant of fast reactors, liquid wastes with a high content of sodium, ash residues from incineration of solid waste, including wood and other vegetation, were effectively immobilized using AASCs (Krivenko *et al.*, 1993).

A following stage development is based on using AACs with low- and non-calcium aluminosilicates. Since the end of the 1970s great attention is paid to AACs of the system Me_2O–Al_2O_3–SiO_2–H_2O termed geopolymers, inorganic polymer cements and geocements which are produced mainly on the basis of ash and metakaolin (Davidovits, 2008; Provis and Deventer, 2009; Juenger *et al.*, 2011; Shi *et al.*, 2011). These types of binders are also called mineral polymers, inorganic polymers, inorganic polymer glasses, alkali-bonded ceramics, alkali ash material, soil cements and hydroceramics.

According to current state of art theory developed using the approach of Glukhovsky (1979), transformation of aluminosilicates into a hardened paste is explained by fragmentation of the starting aluminosilicate materials in the alkali environment with consequent formation of aluminate and low-polymeric silicate anions, which form a highly

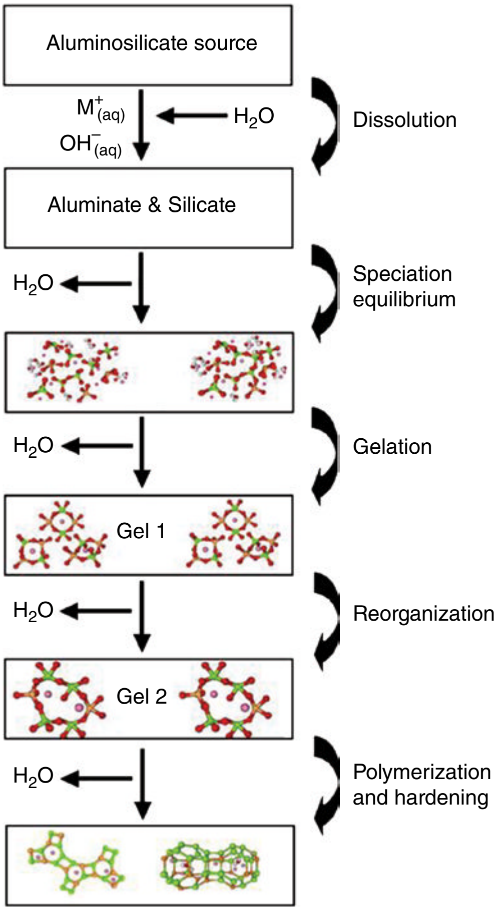

Figure 4.6 *Conceptual model for alkali activation of aluminosilicate. Reproduced with permission from Duxson et al., 2007. © 2007, Springer*

cross-linked aluminosilicate gel ('geopolymer'-type gel) through Si–O–Al–O–Si bonds (Duxson *et al.*, 2007; Davidovits, 2008; Provis and Deventer, 2009). The conceptual model for alkali activation of aluminosilicates developed Duxson *et al.* (2007) is shown in Figure 4.6.

A distinctive feature of the composition of these binders is that the main reaction product is a three-dimensional sodium aluminosilicate hydrate gel, which has as building units alumino- and silica-oxygen tetrahedra (Duxson *et al.*, 2007; Davidovits, 2008; Provis and Deventer, 2009). On a micro- and nanostructure scale the geopolymer gel resembles a zeolite framework (Davidovits, 1991; Duxson *et al.*, 2007) and also can contain some 'crystal' zeolites. As already known, zeolites are formed as a result of crystallization of aluminosilicate gels in hydrothermal conditions (Barrer, 1982). Meanwhile, the crystallization stage passes in these binders only partially and they contain an insignificant quantity of zeolite-like nanocrystals and fully crystallized zeolites (chabazite-Na, analcime, Linde A, etc.) (Provis and Deventer, 2009).

Table 4.4 *Physical–mechanical properties of OPC and geopolymers (special mix designs yield different results)*

Property	OPC	Geopolymer
Compressive strength (MPa)	20–50	34–110
Bending tensile strength (MPa)	2–7	2–20
pH tolerance	6.5–14	3–14
Salt tolerant (continuous exposure)	No	Yes
Max. structural temperature (K)	1090	1533
Curing time (demolding)	1–2 days	3 h to 3 days
Curing time (high strength) (days)	28	3
Curing temperature range (K)	258–489	283–366
Bonds to itself	No	Yes
Bonds to reinforcement	No	Yes
Shrinks upon drying	Yes	No
Coefficient of thermal expansion (1/K)	0.000012	~0.000001
Absorbs water	Yes	No
Foamable	Yes	Yes

The structure, composition and properties of aluminosilicate gel also depend on the structure and amorphization degree of the starting aluminosilicate materials, nature of the alkaline component and curing conditions. The microstructure of the geopolymer obtained by alkaline activation of metakaolin represents a continuous homogeneous gel while the microstructure of slag- and ash-based geopolymers is less homogeneous and contains the substance which has not entered in reaction cemented by gel (Lecomte *et al.*, 2006). At molar ratio Si/Al ~ 2 both the degree of polymerization and water resistance of aluminosilicate gel are maximal, at Si/Al >2–3 there are mainly formed two-dimensional low strength structures (Duxson *et al.*, 2005; Blackford *et al.*, 2007). Formulations with Si/Al ~ 2 are the most suitable based on tests performed using the ASTM/PCT leach test method (Aly *et al.*, 2008).

Crystallization of zeolites in geopolymers is promoted by reduction of the ratio Si/Al<1, by high content of water, high-temperature treatment or long curing time, and on use of alkaline metals hydroxides as activators (Provis *et al.*, 2005).

Table 4.4 shows a comparison of the physical-mechanical properties of OPC and geoploymers (CCHRC, 2010).

Unlike hydraulic binders for which water provides conditions for the structure formation process and is included in the composition of reaction products, water in geopolymers acts as a bearer of the activator, and provides required rheology of fresh paste, and only a small amount of water is chemically bound in reaction products, whereas most of water fills capillary and gel pores (Rahier *et al.*, 1996; Duxson *et al.*, 2005; Skvara, 2007). Generally speaking in terms of macrostructure geopolymers are porous alumino-silicate glasses. This provides the high temperature resistance of the geopolymer, and also its high permeability, and shrinkage during hardening (Provis and Deventer, 2009). The high permeability of geopolymers can be caused by a high water requirement, for example geopolymers based on metakaolin are characterized by a significant surface area (about 1500 m^2/kg, with particle size of 0.5–20 μm). Therefore the water requirement of the binder should be optimized on formulation of geopolymer-based matrixes for immobilization of radioactive waste taking into account the influence of water content on freeze–thaw resistance and radiolysis gas formation. Often metakaolin is preferred when selecting starting components for the development of geopolymers; it is also often used as a model system for the study of formation of structure and the properties of geopolymers. This is due to the fact that unlike waste (slag and ash), metakaolin from different manufacturers is characterized by stable chemical composition, morphology and particle fineness.

The zeolite-like structure of geopolymers provides its high binding ability of the large group of heavy metals and radionuclides, in combination with high physico-mechanical characteristics. This makes them perspective materials for immobilization of low- and intermediate-level wastes. A detailed analysis of studies on the use of geopolymers in this field is presented in Davidovits (2008) and Provis and Deventer (2009). So far, the binding efficiency by geopolymers of 37 elements, including Sr, Cs, Pb, Cr and Zn, has been proved. Leaching from geopolymeric matrix of Cs has been studied by Perera and Trautman (2006) and compared with that of an OPC-based matrix (Hanna *et al.*, 2001). It has been revealed that the diffusion coefficient of boron from a fly ash-based geopolymer is 100 times lower than that of an OPC-based matrix (Palomo and De la Fuente, 2003).

Industrial use of geopolymers for immobilization of radioactive sludges started in Slovakia in 2003 with developed geopolymer formulations accepted by the Slovak Nuclear Authority (UJDSR) and the Czech Nuclear Authority (SUJB) for consequent placement of immobilized wastes in their respective repositories (Lichvar *et al.*, 2010).

Attempts of using geopolymers in the building sector have also been undertaken (Provis and Deventer, 2009).

As well as for matrixes on the basis of other types of cements the use of mixed AACs and the introduction of various admixtures and modifiers allow materials with control properties to be obtained. Combination of non-calcium and calcium aluminosilicates leads to combined microstructure and chemical composition, coexistence of geopolymeric gel and calcium silicate hydrate formation (Yip *et al.*, 2005). It positively affects physico-mechanical properties and the immobilizing properties of matrixes (Van Jaarsveld *et al.*, 2003; Dombrowski *et al.*, 2007; Skvara, 2007).

Combination of slag and metakaolin in equal ratio allows to improve the strength, pore structure and to provide an effective immobilization of copper and lead (Yunsheng, 2004; Yunsheng *et al.*, 2007). Combination of fly ash and slag favours lower permeability of hardened AAC paste and provides immobilization of mercury (Lloyd, 2008).

The introduction of metakaolin to ashes allows to improve the strength and immobilization ability of geopolymer for heavy metals (Van Jaarsveld *et al.*, 2004; Jirasit *et al.*, 2006). Replacement of slag with zeolites or metakaolin increases porosity, but reduces leaching of Cs^+ and Sr^{2+} as a result of the formation of (Al + Na)-substituted calcium silicate hydrate and self-generated zeolites (Shen *et al.*, 1994; Qian *et al.*, 2002). Natural zeolites widely used as sorbents in radioactive waste cementation technology can also be used as an aluminosilicate component of AAC-based matrixes (Cappelletti *et al.*, 2011).

Introduction of staurolite, $Fe(OH)_2{\cdot}2Al_2Si_2O_5$ (0.5–5 mass%) into AASCs based on non-ferrous metallurgical slags of nickel, lead and copper production increases the shielding protective properties of geopolymers for gamma and neutron radiation (Krivenko *et al.*, 1993).

Inert fillers (Fe_2O_3, Al_2O_3, $CaCO_3$, sand, glass) reduce shrinkage and improve compressive and flexural strength (Kuenzel *et al.*, 2011).

The multicomponent composition 'hydroceramics' developed in the USA (metakaolin or ash, 5% vermiculite, 0.5% sodium sulphide, 10% sodium hydroxide) for treatment of sodium-containing wastes consist mainly of zeolites after autoclave treatment (Siemer *et al.*, 2001).

Immobilization of heavy metals and radionuclides depending on their nature can proceed through their physical and/or chemical binding mechanisms. Obviously, there is no universal formulation of a mineral binder-based matrix as the nature of contaminants and compositions of matrixes dictate more or less the specific efficiency.

Geopolymers can be also used as sorbents in waste management technologies. For example, Li *et al.* (2006) developed a foamed geopolymer sorbent based on fly ash and NaOH. The material demonstrated higher adsorption ability on removal of Cu^{2+} from aqueous solutions compared with fly ash and natural zeolite: the adsorption ability of fly ash was 0.1 mg/g, for natural zeolite it was 3.5 mg/g and for geopolymer sorbentit was 92 mg/g (Wang *et al.*, 2007).

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5

Cement Properties, Characterization and Testing

This chapter considers practically important cement properties and methods of cement testing as well as microstructure, phase composition of hardened cement paste and methods of their investigation.

In general, cement properties depend on its chemical–mineralogical composition and fineness; water/cement (w/c) ratio; presence and concentration of additives; and curing conditions. At the same time, the property- and structure formation process and its development are complicated processes caused by the influence of other factors.

5.1 Water/Cement Ratio, Water Requirement, Workability and Water Retention

Water addition to cement actuates the reactions of hydrolysis and hydration of cement minerals to form a solid and strong hardened paste. The content of water used for mixing with cement is one of the key factors influencing the flowability, setting, strength, porosity, permeability, freeze–thaw resistance and finally the durability of hardened cement paste and cement-based materials.

Portland cement even at full hydration at ambient temperature chemically binds 18–23% of water. Therefore the water mixed in cement paste only partially 'chemically' interacts with cement. The quantity of chemically bound water in a month of hardening at 15–20°C is 10–15wt% of cement. On long hardening over tens of years the degree of hydration of ordinary cements (the relation of weight of cement which has reacted with water to the weight of initial cement) does not exceed 0.8–0.9.

Cementitious Materials for Nuclear Waste Immobilization, First Edition. Rehab O. Abdel Rahman,
Ravil Z. Rakhimov, Nailia R. Rakhimova and Michael I. Ojovan.

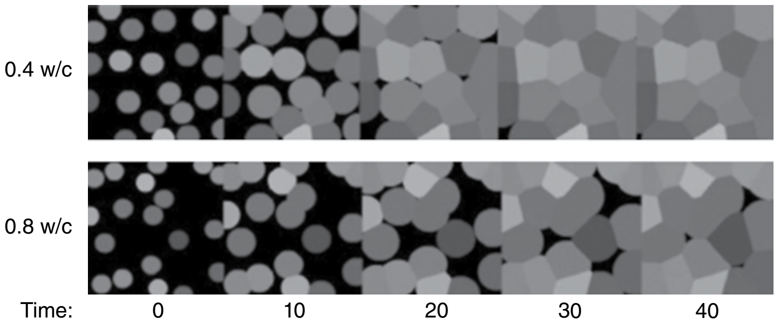

Figure 5.1 *A simple two-dimensional Avramian growth model illustrating the concept of particles impinging on neighbouring particles causing the reaction to slow. Reproduced with permission from Kirby and Biernacki, 2012. © 2012, Elsevier*

The fresh cement paste is a structured system which is characterized by some starting strength. A certain structure is created in the cement paste owing to the forces of molecular adhesion between the particles edged with thin films of water. Liquid phase films create a continuous space network in the structure of the cement paste, giving it the property of plasticity.

As the content of water, as a rule, exceeds that necessary for chemical interaction with clinker, excess water increases the flowability of fresh paste, but at first increases the thickness of layers between reaction products (Figure 5.1) (Kirby and Biernacki, 2012), that in hardened paste interferes further in the formation of continuous structure and strong interatomic bonds, increases its porosity and negatively affects the strength and permeability. Therefore, all other things being equal, the smaller the water requirement of binder, the higher its quality (Volgensky, 1979).

It is worth noting the existence of complex forms of bonds of water with cementitious reaction products. The water is divided into free, chemisorbed or bound by physical forces (sorption) and bound (molecular, crystallization or hydroxyl).

The water requirement of binder is the amount of water to be mixed with cement to form a fresh paste of standard consistency. For various types of cement, the water requirement is 20–30%. The normal consistency of a fresh cement paste is conventionally called the consistency at which the instrument pestle of Vicat's apparatus (Figure 5.2) is immersed in it to a certain depth [by EN 196-3 (1989) standard at 4–8 mm from the glass plate on which the ring device with fresh cement paste is placed].

The water requirement of cement paste increases with the increase of fineness of the cement, calcium aluminate content and the introduction of some mineral admixtures. For example, cement paste water requirement reduction (in order to obtain a more dense and impermeable structure of cement-based materials) can be successfully achieved by the introduction of chemical additives (see Section 3.1).

The w/c ratio of mortars and concretes is in the range of 0.2–0.5. Workability of cement is its ability to fill the mould while keeping its uniformity. It is determined by flowability of concrete and depends on the w/c ratio, type and content of water reducing admixtures. In the technology of concrete and reinforced concrete the workability is set by the moulding process features.

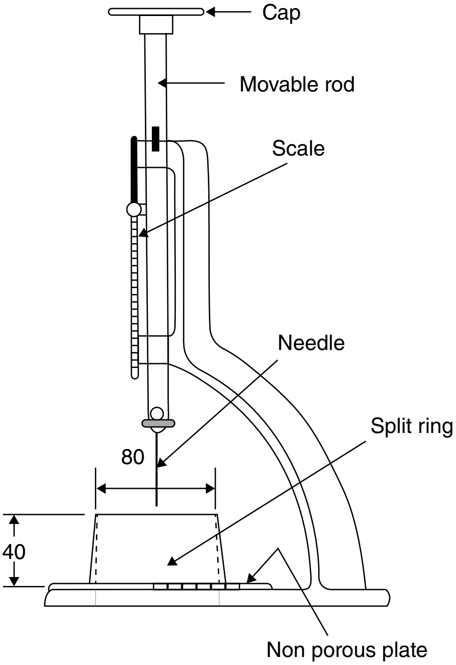

Figure 5.2 *Schematic of Vicat's apparatus (dimensions are given in millimetres)*

Existing radioactive waste cementation technologies require the pouring of cement compounds in containers or drums, therefore mixtures have to have high flowability to fill all voids between solids immobilized. In addition, for liquid radioactive waste a higher waste loading is desired which assumes a higher w/c ratio is used. The higher the w/c ratio, the higher the waste loading and hence the lower the amount of cement needed for immobilization. However the higher the w/c ratio, the higher the conductivity of cementitious wasteform (Figure 5.3) which results in increased radionuclide leaching rates and hence in reduction of corrosion resistance of concrete in aggressive environments (Ojovan and Lee, 2005). Therefore for each specific case the w/c ratio is optimized and mixtures used in practice have w/c ratios typically in the range of 0.3–0.8.

The flowability of cement compounds used for radioactive waste cementation is typically determined by the method and equipment usually used for oil-well cements testing. Fluidity is determined on the device (Figure 5.4), consisting of a cone-shaped vessel mounted on a measuring table with concentric circles printed on it with diameters from 70 to 250 mm. The flowability of cement compounds should be 180 mm (GOST 26798.1-96, 1996).

An important technological property that affects the uniformity of hardened cement paste and the uniformity of distribution of required characteristics in the volume of material is the water holding capacity. It can be reduced when wastes contain oils and resins. Water holding capacity is determined by water separation from cement paste – bleeding. It is assessed by measuring the volume of separated water from cement paste placed in glass cylinders (GOST 26798.1-96, 1996).

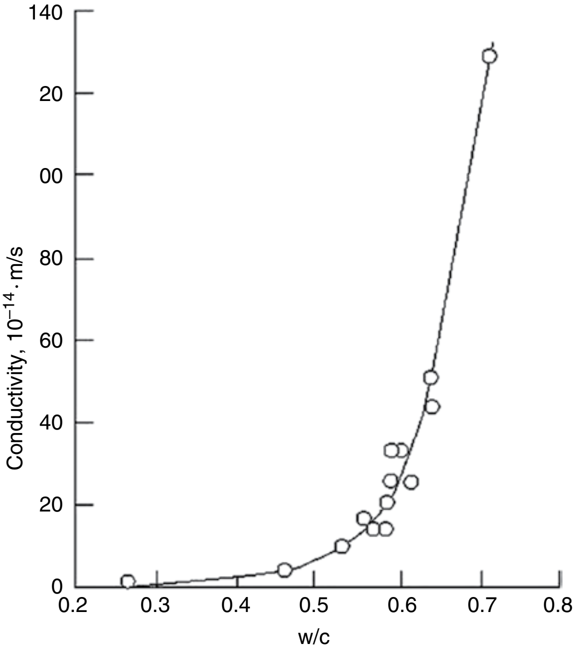

Figure 5.3 *Conductivity of hydrated cement paste as a function of w/c ratio. Reproduced with permission from Ojovan and Lee, 2005. © 2005, Elsevier*

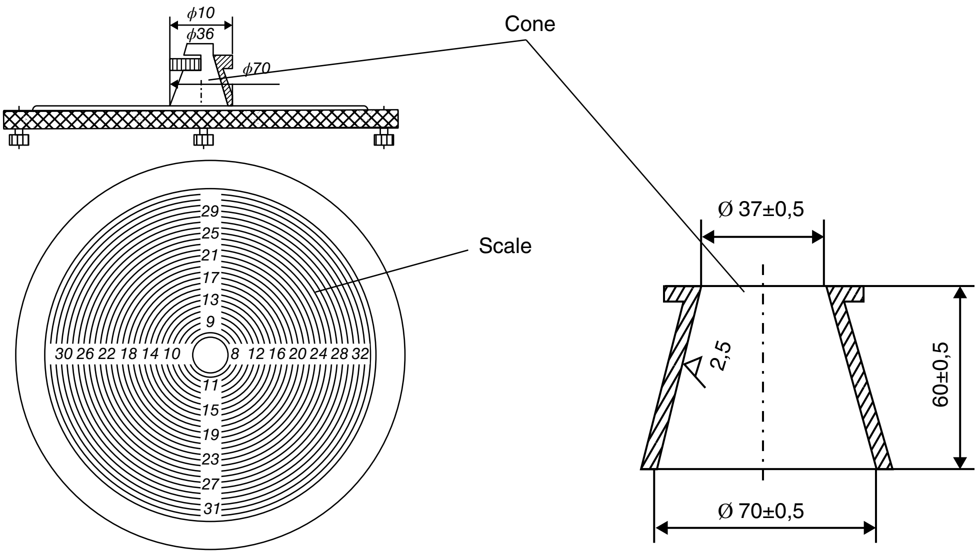

Figure 5.4 *Device for flowability measurement of cement pastes 'AzNII Kr-1 Cone' (dimensions are given in millimetres)*

5.2 Setting Time

Setting and hardening development are of practical importance for binders. Setting is the process of gradual solidification of relatively plastic fresh cement paste, having thixotropic properties, and the acquisition of such starting strength at which its mechanical treatment becomes difficult or even impossible (after setting). Therefore, binders, including cement, should be characterized by setting time providing their possible mixing and placing of mixtures before their complete solidification (final set time).

Cements are characterized by initial and final setting time. The setting time of cement can be determined by Gillmore (ASTM C 266-08e1, 2008) or Vicat's apparatuses (EN 196-3, 1989; ASTM C 191, 2008). The difference between these two methods is due to the size and weight of needle used. The ASTM C 266 test protocol requires the beginning of setting to occur not earlier than after 60 min and finish not later than after 10 h (Gillmore); the EN 196-3 (1989) (Vicat's) gives the beginning at greater than 45 min and the end to be less than10 h.

In the Gillmore method, a pat of cement paste 3 in. in diameter and 1/2 in. thick is formed on a glass plate and is subjected to indentation by the needle. For the initial set the needle weighing 1/4 lb with 1/12 in. diameter is used while for the final set the corresponding figures are 1 lb and 1/24 in. The initial set occurs when the pat will bear without appreciable indentation, the initial Gillmore needle. Similarly, the final set is determined by the final Gillmore needle. All standard ASTM cements should conform to an initial setting time not less than 60 min and final setting time of not more than 10 h.

The corresponding times using the Vicat needle are 45 min and 8 h. The Vicat's apparatus is similar to the test method described above except that there are slight differences in the needle weight and diameter and the dimensions of the cement paste. In this method, the initial setting time occurs when a penetration of 25 mm is obtained. At the time of final set the needle should not sink visibly into the paste.

According to EN 196-3 (1989) initial setting time occurs when a penetration of 1–2 mm is obtained. At the time of final set the needle should not sink visibly into the paste.

Other methods are also involved in studies of cements for determining the setting time (Trtnik *et al.*, 2008; Ylmén *et al.*, 2009; Trtnik and Gams, 2013; Wang *et al.*, 2013).

Setting time depends on many factors and can be regulated within a wide range. Setting time shortens with the increase of calcium aluminates content and fineness, temperature increase and decrease of w/c ratio.

The most important regulator of setting time of ordinary Portland cement (OPC) is gypsum dihydrate, which is introduced in the grinding of OPC in the amount of 3–6%. Moreover, the percentage of gypsum predetermines not only the setting but the most important properties such as strength, strength development, shrinkage, and freeze–thaw resistance.

The mechanism of lengthening of OPC setting time in the presence of gypsum is as follows: according to studies summarized in Volgensky (1979) when mixing OPC with water regardless of gypsum presence shielding shells are formed on the surface of cement particles consisting of hydration products, which lead to the cessation of interaction of binder with water and initiate the so-called induction period. In the absence of gypsum the shells formed are voluminous and friable consisting of calcium aluminate hydrates. They are connecting particles in a uniform albeit weak structure of initial hardening. In the presence of gypsum thin shells containing tiny ettringite particles are formed on the surface of clinker particles.

These form in some hours extended crystals which gradually connect particles with each other causing the setting effect of cement paste. Owing to recrystallization the shells become more permeable to water which causes strengthening of their interaction with cement and leads to a further hardening of structure.

Similar shielding shells at the initial stage of interaction with water are also observed for other binders.

Bensted (1983) has found that during the setting period the fraction of ettringite practically does not increase, therefore ettringite formation cannot be considered as a principal cause of full loss of mobility of water in the cement paste. Formation of OH^- associates, water and ions, forming the anisotropic structure of gels has been observed at the moment of loss of workability of cement pastes. Detailed study of hydrate formation processes during the setting period has revealed that setting of OPC is caused mainly by immobilization of water by calcium silicate hydrate (C–S–H) phases.

An important role in the formation of such properties of cement as water requirement and setting time is played by the concentration of active centres in clinker minerals. The quantity of the primary active centres depends on clinker thermal history, for example, burning and cooling conditions and type and quantity of alloying additives. Secondary active centres are formed on the surface of hydrated phases. Electrokinetic characteristics of watered cement particles are directly connected to the concentration of these active centres, regulating to a certain degree coagulation processes in cement gel (Paschenko *et al.*, 1991). Recent studies (Dvorkin and Dvorkin, 2011) have shown that the mechanism of influence of gypsum is connected to the change in concentration of active centres in cement grains. Active centres also affect coagulation processes.

The experience of radioactive waste cementation shows the necessity of introducing in cement compounds cement setting retarders or accelerators in terms of sensitivity of OPC to phosphates, chlorides, sulphates, formates, borates and so on. Table 5.1 lists the reactions which take place on interaction with components of some wastes (Ojovan and Lee, 2005).

The impact of cations on cement hydration reactions follows the series:

$$Ca^{2+} > Ni^{2+} > Ba^{2+} > Mg^{2+} > Fe^{3+} > Cr^{3+} > Co^{2+} > La^{3+} > NH_4^+ \\ > K^+ > Li^+ > Cs^+ > Na^+ > Cu^{2+} > Zn^{2+} > Pb^{2+},$$

Table 5.1 *Reactions occurring between cement and waste components*

Waste component	Reaction
Soluble borates, Pb, Zn	Precipitated salts coat cement grains or amorphous precipitates inhibit hydration
Complexing agents: EDTA, sugar, citric acid	Interfere with Ca availability by complexation. Retard hydration
Flocs	Uncertain action. Retard hydration
Electropositive metals	Evolve H. Reaction accelerated by OH^-. Solid reaction products, oxides/hydroxides are expansive
Organic ion exchangers	Take up water in high pH matrices and expand

whereas anions follow the series:

$$OH^{-} > Cl^{-} > Br^{-} > NO_3^{-} > SO_4^{2-} >> CH_3COO^{-}$$

To overcome deleterious cement–waste interaction effects, one or more additives may be used and such mixtures are termed modified cements. Several of the more successful modified Portland cements have been commercialized (Ojovan and Lee, 2005).

5.3 Specific Surface Area and Particle Size Distribution

The powdery state of cement predetermines the relationship between particle size and interaction development with water, properties of fresh and hardened cement paste. The fineness of grinding of cement is one of the key parameters allowing to control reactivity of cement, setting time, strength and strength development, permeability of hardened cement paste and so on. The fineness is characterized by specific surface area and particle size distribution.

In the cement industry the specific surface area (total surface area of cement grains in m^2/kg) is often determined using Blaine apparatus based on air permeability of material (Blaine, EN 196-6). This method is based on the measurement of resistance which renders a packed layer of cement to air which is pumped through it. The powder is packed in a special sleeve (bushing) and contains a system of channels of various cross sections which are smaller for finer ground powders. Having determined the air permeability of such a system, it is possible to calculate a conditional specific surface of cement with some assumptions. The time during which a certain quantity of air passes through the cement layer under given conditions is measured, and the specific surface is calculated accounting for air permeability of the layer, porosity of material, its density and viscosity of air.

Another method for determination of the specific surface area is the Brunauer–Emmett–Teller (BET) method in which the phenomenon of gas adsorption is used. Measuring the quantity of adsorbed nitrogen at −196°C at various partial pressures of nitrogen it is possible to calculate the capacity of a monolayer and then of the specific surface. Typical specific surface areas for contemporary OPC are 300–350 m^2/kg whereas for fast-setting cements they are in the range of 400–450 m^2/kg (Blaine). It is necessary to take into consideration that the BET method gives results which exceed the values obtained by the air permeability method by two- to threefold as it measures all surfaces, including the surface of opened pores from only one side and internal surfaces of microcracks (Taylor, 1997). The relative difference between a specific surface area obtained by Blaine and BET methods can give important information regarding agglomeration and flake formation (Opoczky and Verdes, 1986).

A very important characteristic of cement is the granulometric composition. Optimization of granulometric composition is more effective to control the properties of cement than regulation of the specific surface area (Sychev and Svatovskaya, 1983).

There are different methods for testing particle size distribution, giving different results (Taylor, 1997). The most used methods are (De Weerdt, 2013):

- mechanical sifting by means of a set of sieves;
- air-swept sifting;
- laser granulometry;
- electric granulometry.

The additional information about granulometric composition of cement can be obtained with the application of optical microscopy and scanning electron microscopy (SEM).

For the description of granulometric composition a two-parametrical mathematical model is often used – Weibull distribution or Rosin–Rammler–Sperling–Bennett (RRSB) function $R(x)$ (Taylor, 1997; Locher, 2006):

$$\frac{1}{R(x)} = \exp\left(\frac{x}{\sigma}\right)^n,$$

where $R(x)$ is the mass fraction of particles larger than x;
x is the diameter of particles in mm;
σ is the characteristic size of grain, over which 36.8wt% of particles contain.

Comparison of granulometric compositions is made in terms of two parameters of function $R(x)$:

- characteristic size of grains σ, 'displaying' the fineness of a grinding;
- uniformity index of particle size distribution n, 'displaying' the degree of dispersion of particles by their sizes (the higher n the narrower range of particle sizes).

The role of particle size and optimum particle size distribution of cement are under research attention. In general, fine particles provide early strength, however there is high water requirement and undesirable changes in volume due to the fast hydration. With increase of hardening duration of cement paste its strength development depends on the average size of particles. Large particles play the role of fillers and do not essentially contribute to strength development (Tsivilis *et al.*, 1990). Many studies (Butt, 1974; Sumner *et al.*, 1986) found that the 1-day age cement strength depends on the content of fraction <5 μm, 3- to 7-day age on 5–10 μm, 1 month and more on 10–20 μm, and 90- to180-day age on 30–40 μm. Particles larger than 40 μm affect strength increase only after some years.

Ivanov-Gorodov (1960) stated that uniform and fast hardening is reached at the following granulometric composition: <5 μm, 15–20%; 5–20 μm, 40–45%; 20–40 μm, 20–25%; and >40 μm, 15–20%.

Tsivilis *et al.* (1990, 1998) proposed the following optimum particle size distribution: <5 μm, 15–20%; 5–20 μm, 40–45%; 20–40 μm, 20–25%; and >40 μm, 15–20%. The content of particles with size 3–30 μm can be above 65%, and the content of particles with sizes >60 μm and <1 μm should be as small as possible.

It is important to take into consideration, that increase of early strength with increase in the content of fine particles is caused not only by acceleration of hydration reactions owing to increase of specific surface area and increase of surface activity, but also with non-uniform distribution of Portland clinker minerals and gypsum which depends on size of particles. With increase of particle size the content of rapid-hydrating alite decreases, and belite content increases (Gutteridge and Dalziel, 1990) whereas particle size effect on aluminate and ferrite phases content is negligible. Lingling *et al.* (2011) have studied the chemical composition of narrow particle size fractions of OPC and found that the large particle size fraction has an increased content of SiO_2, Fe_2O_3 and MgO, while the small particle size fraction has an increased content of SO_3. The content of C_3S in the 0–3 μm size fraction was 73.5%, and of C_2S 8.1%. Therefore particles with size 3–15 μm have a higher contribution to the 3-day age strength, and those with size 16–30 μm to the 28-day age strength. Osbaeck and Jons (1980) stated that in the most finely ground cement fractions gypsum and its dehydration products concentrate. Each 1% of gypsum brings about 10 m^2/kg to cement specific surface and generally about 15% of total specific surface is formed owing to gypsum.

The properties of cement can be also regulated by variation of width of a granulometric composition. Narrowing of area of cement particles distribution increases the degree of hydration by 28 days (Frigione and Marra, 1976; Sumner *et al.*, 1986), therefore strength improvement is possible by use of cements with narrow granulometric composition. OPCs with wide granulometric composition have even over long time periods a certain quantity of unhydrated particles. Microscopic analysis of OPC-based concrete blended with 20% of bergmeal hardened under water over 36 years showed the presence of about 25% of unreacted clinker minerals mainly belite and aluminoferrite (mainly C_2S, C_4AF). Analysis of samples of OPC-based concrete, hardened in air in natural conditions over 15 years showed that in these samples there is 40% of unhydrated particles (Shestoperov, 1977).

An increase in efficiency of use of Portland clinker minerals is also via replacement of large cement particles with mineral admixtures of similar size. Bentz (2005) established that replacing cement particles larger than 30 μm by ground limestone of equivalent size at $w/c = 0.3$ does not considerably affect the strength for ages up to 56 days.

There are finely ground cements and binders with low water requirement with specific surface area larger than 450 m^2/kg. Fine-ground cements are used for immobilization of solid radioactive wastes by impregnation. High-penetrating mortar for fine-dispersed radioactive wastes is prepared using fine-ground cement with specific surface area 1000–1200 m^2/kg, for close-packed disperse wastes and 600 m^2/kg large-size wastes or in the last case OPC with fine-ground cement as admixture (Varlakov, 2011). However in using finely milled cements the diseconomy of superfine grinding and its negative influence on freeze–thaw durability, sulphate and heat release, shrinkage and durability of cement-based materials should be taken into account.

Noteworthy is the question of influence on rheology, workability, setting, and strength of OPC particle shapes. Along with the traditional ball mills, over the past decade other methods of clinker milling have been developed and put into production. The technical solutions that have appeared in the cement industry include vertical roller mills, press rolls and combinations of high pressure press rolls. This equipment can be classified according to the manner of destruction of material, for example compression, shear, impact or friction, although often it is difficult to separate them based on unique force such as milling which uses two types of force at least. In addition on destruction of material there are three types of fragmentation, namely grinding due to abrasion, chipping and bulk destruction which occur more or less simultaneously (Locher, 2006).

5.4 Heat Evolution

It was noted (Section 2.5.1) that hydration reactions of clinker minerals are exothermic, for example the interaction of OPC with water is accompanied by heat release. The heat release depends on chemical–mineralogical composition, fineness of grinding and presence of admixtures. It is worth noting that calcium aluminate cements and calcium sulphoaluminate cements surpass OPC in heat emission (see Chapter 4, Figure 4.2). Cement heat release at hydration requires control as the consequences of it are not always positive. On concreting at low temperatures the heat release gives the opportunity to extend mixture cooling time, assist hydration and delay water freezing in pores and capillaries. In contrast, erection of massive structures from OPC-based concrete with raised heat release causes overheating to 50°C and above, and on subsequent cooling considerable differences in temperature between external and internal zones occurs, which can result in stretching pressure and formation of cracks within surface layers. To decrease heat release from OPC-based concrete structures, they are 'diluted' with mineral admixtures.

Heat evolution is quantified in Joules per gramme of unhydrated cement released at its full hydration at a certain temperature. The most widely used method of heat evolution testing is through measuring the heat of solution of unhydrated and hydrated cement in a mixture of nitric and hydrofluoric acids: the difference between two values obtained represents the heat evolution at hydration. The method of heat evolution testing by calorimetry is presented for example in EN 196-8 standard.

The total heat evolved is the sum of heat evolution during chemical reactions and heat evolution resulting from water sorption by surface gel formed in the course of hydration. The heat of sorption usually makes up one-quarter of total heat release. For practical purposes it is not necessary to know the total heat evolved but rather the rate of heat evolution which can be readily measured using an adiabatic calorimeter.

5.5 Strength

Strength is the pressure on area unit of initial cement paste or mortar sample section which causes its destruction at the externally applied compressing, stretching or bending loadings. From a structural point of view hardened cement paste is a multilevel highly heterogeneous system consisting of solid and liquid phases and pores. Each of these structural elements is diverse in their molecular, micro- and macrostructural characteristics affecting to a greater or lesser extent the structure formation process and strength development. Table 5.2 lists factors determining strength of hardened cement paste.

The factors listed differently determine the degree of hydration clinker phases, phase composition and the microstructure of hardened cement paste which in turn determine its physical properties, including strength. On hardening of monomineral mixes the highest early strength is demonstrated by C_3S, and the lowest by C_2S (Section 2.5.1). The monomineral hardened paste obtained from C_3A shows low strength at long times of hardening. Samples of C_4AF have higher strength than C_3A-based materials but not as high as hardened paste from C_3S. At long times of hardening (>6 months) the monomineral paste obtained on the basis of C_2S has high strength. The strength of the hardened polymineral cements does not obey the additivity law as other factors significantly affect physical structure of cement paste besides mineralogical composition. Strength of cement paste is unambiguously determined by its physical structure, therefore strength characteristics functionally connect it either with concentration of hydrated solid phase or with porosity of a material (Figure 5.5) (Butt *et al.*, 1980).

Many researchers stated that identical degree of hydration of OPC is an important condition to achieve commensurable strength values for samples of a cement paste of different

Table 5.2 Factors determining strength of hardened cement paste

Volgensky (1979)	Taylor (1997)
Properties and content of binder in unit of volume of an initial mix with the water, causing initial starting porosity of system	Cement characteristics, such as composition and a clinker microstructure, content of gypsum and particle size distribution
The content (concentration) of unhydrated binder and hydrated reaction products in the volume of hardening paste, depending on degree of hydration (both determining character and volume of its pores)	w/c, air and additives presence
Properties of hydrated reaction products particles, predetermining the microstructure of hardened system (degree of condensation silica-oxygen anions, fineness and configuration, reflected by specific surface, adhesive and cohesive properties, strength of particles, etc.)	Mixing condition
Specific heat, hydration rate and heat release of binders	Curing conditions, especially temperature and relative humidity
Temperature of hardening mixture of binder with water and aggregates	Age
Character of hardening process environment (water and vapours-gas) (in particular, presence of aggressive substances)	Testing method, including the content of water in the sample
Presence in the hardening mix of various additives (regulators of setting and hardening, plasticizer, waterproofing admixture etc.)	

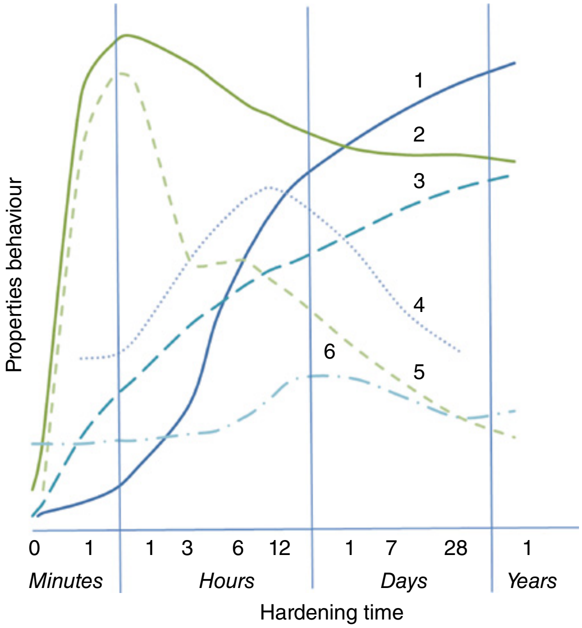

Figure 5.5 *Properties of fresh and hardened cement paste versus age: 1, strength; 2, pH; 3, degree of hydration; 4, temperature (and heat evolution); 5, electroconductivity; 6, porosity. Reproduced from Butt* et al.*, 1980*

composition obtained at different curing conditions. At identical chemical and phase composition physico-mechanical properties of cement paste can essentially vary depending on geometrical parameters of reaction products and pores characterizing its microstructure (Paschenko *et al.*, 1991). Porosity of cement paste is an important factor in the formation of strength and other operational characteristics, for example freeze–thaw durability and corrosion resistance. Of great importance is the homogeneous distribution of porosity and reaction products in the volume of material. Characteristics of pore structure of cement paste depend on w/c ratio, method of consolidation (e.g. vibrating, pressing, moulding), curing conditions and age. The mineralogical composition of cement also has an influence on pore structure creating the relationship between hydrated phases (Paschenko *et al.*, 1991). Uchikawa (1984) classifies pores depending on their influence on physico-technical properties of cement paste as follows:

1. Pores with diameters ≥2 μm, and those with sizes of a few nanometres and smaller are important for the stability of structure at freezing–thawing.
2. Pores with diameters from several tens to hundreds of nanometres determine gas and water permeability and have an effect on neutralization of a cement paste by carboxylation.
3. Pores with diameters of some tens of nanometres determine diffusion and transport of ions and have an effect on chemical resistance to sulphates and chlorides; they also determine stability of interaction between cement bases and cement aggregates.

An increase of total porosity of a cement paste from 10 to 60% significantly decreases its strength (Bajenov, 2002). Locher (1976) has systematized the experimental data of Verbek and Helmut (1968), Judenfreund *et al.* (1972a, 1972b), Roy and Gouda (1973) and Feldman and Beaudoin (1976) on the strength and porosity of normally consolidated cement paste steam cured at normal pressure. Figure 5.6 presents results of this analysis.

Capillary porosity was determined by known porosimetry methods or by calculation on the basis of the initial w/c ratio and degree of hydration on the assumption that the crystalline hydrates bond of cement paste has a constant porosity of 28% and constant specific volume of solid phase of about 0.4 cm^3/g. The lowest capillary porosity is close to zero and the highest compressive strength of cement paste is 200 MPa. These results were obtained by Judenfreund *et al.* (1972a, b) as a result of high fineness clinker with specific surface area of 6000–9000 cm^2/g using vibrocompaction, low w/c ratio and superplasticizer.

The strength of cement paste at the same degree of hydration and porosity depends on the character of crystallization of hydrates which fill large pores. Many studies have found that agglomeration of hydrate particles and increase of their degree of crystallization decrease the strength of cement owing to a reduction in number and area of contacts between crystals. The densest mass of hydrates with high number of contacts between particles is formed in poorly crystallized cement gels. In this case the strength of cement paste is high and especially with high porosity. The highest strength of a dense cement paste is reached at an optimum combination of poorly crystallized mass of hydrates with dense and well crystallized parts. Poorly crystallized mass acts as the binding function, cementing unhydrated clinker particles and large crystal hydrates such as portlandite and ettringite. Binder gel consisting of calcium silicate hydrates has the strongest binding properties. The crystalline calcium aluminate hydrates in it reduce its binding ability. Formation

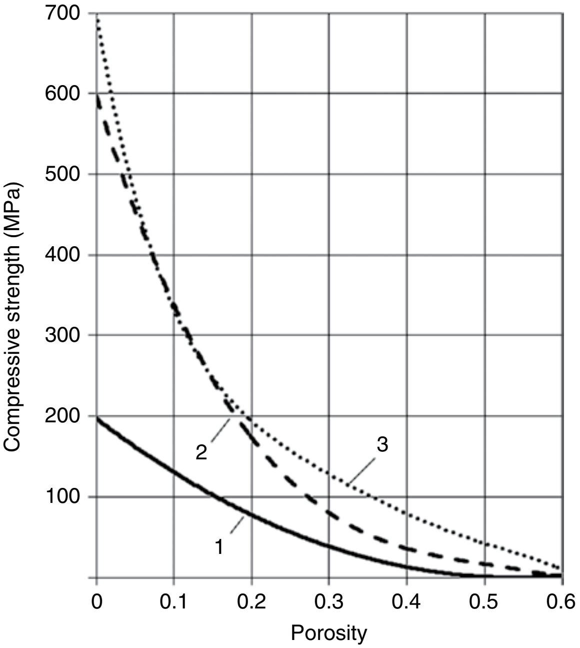

Figure 5.6 Compressive strength of cement paste versus capillary (1) and total porosity (2, 3). Reproduced with permission from M. Babkov

of long-fibre calcium silicate hydrates is favourable to block cracks or large pores; this is especially effective in the case of the formation of dendroid-like joints by such fibres (Butt *et al.*, 1980).

The binding ability of high-basic C–S–H phases reflected in the compressive strength of cement paste is 2.5–3 times lower than that of low-basic C–S–H phases. This is due to the fact that high-basic calcium silicate hydrates have more (Si–O–Si)-type covalent bonds and less weaker ionic (Ca–O–Si)-type bonds (Timaschev, 1978). Cement pastes containing more dense and crystallized reaction products with reduced degree of fineness have higher strength (Kurdowski *et al.*, 1986).

Though porosity is a major factor controlling strength, Feldman and Beaudoin (1976) drew the conclusion that the morphology and density of particles are also important. At high porosity adhesion of particles increases the strength of poorly crystallized material and at low porosity higher strength is provided by the strength of dense crystalline particles. Based on studies of cement pastes cured at different w/c ratio, temperature and time, Odler and Rößler (1985) concluded that strength increases with increase of content of hydrated phase, and that the influence of pores with radii less than 10 nm is negligible. Thus, the strength of cement paste which mainly depends on content of hydrates and porosity markedly changes with varying content and degree of crystallization of hydrates. Crystallization of hydrates changes depending on many factors, for example hardening temperature, impurity content and fineness of cement (Butt *et al.*, 1980).

Bound water plays an important role in strength formation of cement paste. The C–S–H phase contains interlayer cavities with sizes from 0.5–3 nm to 1 μm. Cavities of 0.5–3 nm contain strongly bound molecules of water. The water films filling interlayer spaces reinforce the paste providing strong interaction between layers. Intercrystalline cavities with sizes of the order of 3–10 nm in poorly crystallized parts of C–S–H keep the adsorbed water. This type of water is more ordered than free water however the binding energy of this type of water with intercrystalline surfaces is weaker than that of interlayer water of C–S–H (Paschenko *et al.*, 1991).

Varying hydration states, that is water content of C–S–H, AFm and AFt phases may have a direct impact on the specific density/volume of cement paste. For example, the volume of some hydrates can change as much as 20% during drying and may thus strongly affect the porosity and performance of a cementitious system (Baquerizo *et al.*, 2012).

Strength increase of a cement paste can be achieved through formulation of optimal particle size distribution, reduction of w/c ratio, introduction of chemical and mineral additives, impregnation by polymers and oligomers, pressing, elimination of conditions for occurrence of nonuniformity and defects of structure.

Strength characteristics are the basic criteria in assessing the quality of cement.

Quality can be expressed both as the average strength and the level of variation. In the EN 197-1 (2000) cement performance standard the average and variation are combined in what are called the L- and U-values. The L-value describes the level where 95% of the strength population is higher and the U-value where 90% of the population is lower. It could be argued that the L-value could be used as an indicator of customer value. Competent concrete producers with effective processes set more stringent requirements on cement products. By way of example, Swedish customers require that cement final strength varies by no more than ±4 MPa around a set target. This can be compared with the maximum range specified in the standard of ±10 MPa (Koski *et al.*, 2011).

According to EN 196-1 (1989) the cement strength testing is as follows: a mortar containing cement, water and CEN Standard sand with $w/c = 0.50$ is mixed in a mixer. Each mix consists of 450 g cement, 225 g water and 1350 g sand. The mortar is moulded in steel moulds after mixing with one mix filling one mould. The steel mould consists of three compartments, so that three prismatic specimens ($40 \times 40 \times 160$ mm), hereafter called mortar bars, are moulded at the same time. The moulds are filled and the compaction is performed by a jolting table. After filling, compaction and removal of excess mortar, the moulds are placed in a moist cabinet (20 ± 1°C, >90% RH) for 24 h. The specimens are cured in water (20 ± 1°C) for 28 days. Then samples are tested on compressive and bending strength.

Non-destructive methods can be also used for characterizing the strength of cement paste and concrete. The classical approach to mechanical properties relies on compressive strength evolution over time. These data sre increasingly complemented by (Stark, 2011):

- numerical simulation based on finite element approaches and other methods;
- wave emission and propagation;
- nanoindentation methods.

Acoustic emission is also a powerful passive method to detect the early development of cracks in cementitious wasteforms and characterize the reliability of waste immobilization (Spasova and Ojovan, 2008).

5.6 Freeze–Thaw Resistance

Freeze–thaw resistance is the ability of a material to hold in a waterlogged state with alternate freezing and thawing conditions which is the main criterion of an assessment of durability of artificial stone materials. Among those most often used in modern building are concrete and reinforced concrete. The criterion of freeze–thaw resistance of concrete is the number of cycles at which the sample loss in weight is less than 3% and its strength decreases by not more than 15% for light-weight and 5% for heavy concretes (GOST 10060.1-95, 1995). The number of cycles defines the concrete mark on frost resistance, for example for heavy concrete it is 50–500.

Destruction of artificial stone materials at low temperatures is caused by ice formation in pores of the material on water freezing and cyclic pressure on pore walls.

The water of cement paste which contains a certain amount of $Ca(OH)_2$ and dissolved alkaline compounds freezes to ice first in large pores and cavities at temperatures of 0 to −1°C. On further decrease in temperature ice starts to form in capillaries with smaller diameters. In the thinnest capillaries the water freezes only near −25°C whereas in gel pores, according to some data, only at −70°C. Under the pressure of freezing water and ice on pores and capillary walls the cement paste considerably increases its volume. This increase especially at temperatures from −5 to −20°C reaches about 1–2 mm/m depending on the properties of the cement and the w/c ratio. On thawing the volume decreases but does not return to its initial value.

The freeze–thaw resistance of a cement paste depends on its total porosity and on its character. The smaller the total porosity, the higher the freeze–thaw resistance. Reduction of the total porosity is obtained by increase in the degree of hydration of cement, decrease of w/c ratio and long term hardening before the beginning of cycles of alternate freezing and thawing during which capillary pores are filled with hydrated reaction products (Volgensky, 1979; Ramachandran and Beaudoin, 1990).

According to many researchers frost damage is not necessarily connected with the expansion of water during freezing although it can contribute to damage. Although many organic compounds such as benzene and chloroform contract during freezing they nevertheless can cause damage during the freezing transition. When a water-saturated porous material freezes, macroscopic ice crystals form in coarser pores and the water which is unfrozen in finer pores migrates to the coarser pores or to the surface (Everett, 1961). The large ice crystals can feed on the small ice crystals, even when the larger ones are under constraint.

A quite effective and relatively simple method to increase freeze–thaw resistance is based on the introduction of air-entraining agents (Figure 5.7). To obtain a freeze–thaw resistant concrete the distance between air pores, that is the thickness of layers between adjacent pores, must not exceed 0.025 cm (Bajenov, 2002). Therefore for an appropriate effect it is necessary to provide not only a certain entrained air volume, but also the formation of air pores of possibly smaller sizes as this would allow their total volume to be reduced and promote the increase of freeze–thaw resistance of concrete with the least reduction in strength owing to air entraining. Usually concretes with air-entraining agents have a specific surface of pores in the range of 1000–2000 cm^2/cm^3 and pore sizes in the range of 0.005–0.1 cm with distances between them not exceeding 0.025 cm (Bajenov, 2002). A spherical pore plays a role of spare capacity in which the water is squeezed out on expansion from capillaries during the water–ice transition. It is interesting to notice that cements with a considerable volume of air pores do not increase their volume but reduce their volume by a magnitude which corresponds to the

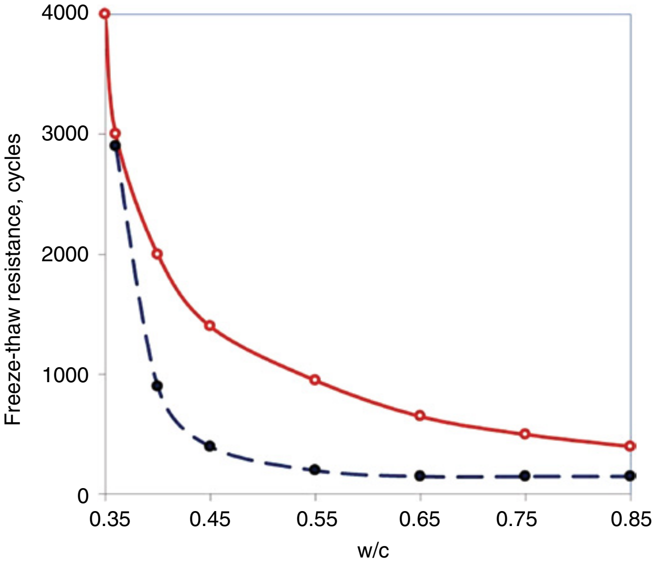

Figure 5.7 *Freeze–thaw resistance of concrete with entrained air (1) and reference concrete (2) as a function of w/c ratio*

temperature difference at the corresponding factor of thermal compression. The volumes of such cements nearly return to their initial volumes on subsequent thawing (Volgensky, 1979).

The same effect as introducing air entraining agents which results in the formation of spare capacities is achieved with the introduction of polymeric microspheres and porous particles. It has been shown that addition of particles which correspond to less than 2% equivalent air is similar to conventional air-entrained concrete containing 5% air (Sommer, 1977; Litvan, 1978). Control of the right size and spacing of air pockets in these particles can add to the effectiveness of cement against frost action.

Other ways to improve freeze–thaw resistance is through increasing concrete density, reduction in volume of macropores and their permeability with respect to water, for example, via decrease of w/c ratio, introduction of additives and waterproofing pore walls by impregnation by special compounds. The cement paste does almost not contains capillary pores at w/c = 0.4–0.45 and high hydration. Its porosity is created basically by gel pores filled by water in a pseudo-solid state. From here it follows that high freeze–thaw resistant concrete can be prepared at w/c ratios not exceeding 0.45–0.5. Thus it is reasonable to use water reducing additives. Waterproofing additives complicate suction of water into cement paste and its motion. In addition they promote an increased number of closed pores which are not filled with water at the usual saturation of concrete (Volgensky, 1979; Bajenov, 2002).

The most widely used test for assessing the resistance of concrete to freezing–thawing is the ASTM Standard test method for resistance of concrete to rapid freezing and thawing (ASTM C666/C666M, 2008). This method uses two different procedures: in Procedure A, both freezing and thawing occur with the specimens surrounded by water; and in Procedure B, the specimens are frozen in air and thawed in water. Procedure A is somewhat more reproducible than Procedure B.

5.7 Microstructure and Analysis

Hardened cement paste is characterized by the complexity of composition, the diversity of structural elements by form and size. The hardened cement paste produced by the interaction of Portland or blended cement with water is composed of anhydrous phases (unreacted clinker minerals, mineral additions), hydrate phases modified by foreign ions incorporation and adsorption (C–S–H, ettringite, portlandite, AFm), minor phases such as hydrotalkite, pore solution and pores (Stark, 2011). As the most important properties of cement-based materials such as strength and durability depend on features of both solid and non-solid phases (Section 2.3.3), a lot of attention is given to the investigation of cement microstructure. The state of the solid phase of a cement paste, its composition and structure depend on many compositional and technological factors and can undergo essential changes with increase of hardening duration and under the influence of external factors. The solid phase contains a certain quantity of unhydrated cement, calcium silicate hydrates, calcium hydroxide, hydration products of calcium aluminate and aluminoferrite. Reaction products of cement essentially differ in terms of composition, form and size. The C–S–H is characterized by the existence of various forms including foil-, flake, fibre- and tubular-like (Davies *et al.*, 1989).

Portlandite crystals have the form of hexagonal prisms. Calcium sulphoaluminate hydrates have hexagonal-lamellar and hexagonal- prismatic forms or are seen as needle-like structures. Crystals of ettringite can be as long as 120 μm and be 2–3 μm thick. The usual size of hydro in calcium silicate hydrates is 2.0 μm, and in calcium hydroxide crystals is 100 μm and above (Van Breugel, 1991).

Most attention is given to the C–S–H phase on account of its contribution to the formation of the basic physico-mechanical properties of cement paste. Its basic characteristics are: its chemical composition (CaO/SiO_2 and H_2O/SiO_2 ratios); presence of impurities of Al, Fe, Mg, K, Na, S; anion structure (degree of polymerization of silicate anions); and morphology (the size of reaction products and crystallinity). In addition, calcium silicate hydrates are divided into 'inner' and 'outer', 'early' and 'late', with different CaO/SiO_2 ratios, by density and so on (Figure 5.8) (Taylor, 1997; Stora *et al.*, 2009; McDonald *et al.*, 2010). It is still difficult to study this phase due to its variable chemical composition, lack of a true long range order, its very high surface favouring absorption of foreign ions, and sensitivity to vacuum, elevated temperature and carbon dioxide. Progress has been made in the characterization of this phase with respect to its nanostructure, thermodynamic properties, solubility (including the impact of aluminium incorporation), electron binding energies, morphology, adsorption, intercalation of organic molecules and mechanical properties (Stark, 2011).

It is important to note the increasing role of modelling augmented with experimental methods of research of composition and structure allowing the development of the theoretical basis of the formation and structure of cement paste for all its length scale levels (see Table 5.3 which lists current methods of analysis of the composition and structure of cements). One of the latest roles of modelling is in miniaturization, developing models at increasingly lower size levels. Much of this new perspective must be attributed to researchers such as Kalinichev, Kirkpatrick, Scrivener, van Damme and Pellenq who recognized that it is the nano-scale structure of cementitious materials that is responsible for cohesion and durability (Dolado and Van Brougel, 2011). Therefore, the next source of improvement of cement-based materials would lie in the fine-tuning of the nanoscale hydrates and colloidal

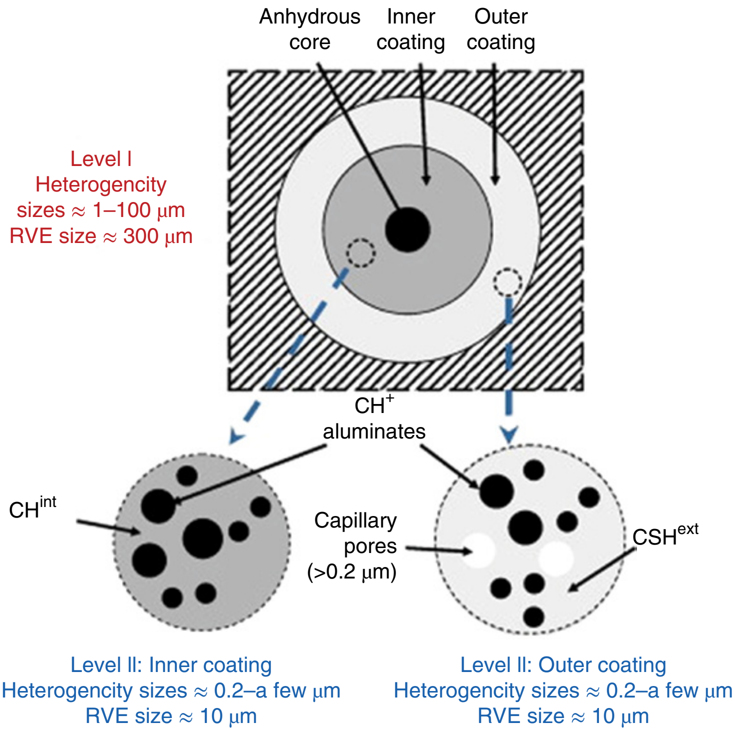

Figure 5.8 *Schematic of levels I and II of the multiscale representation used for the estimation of the effective elastic and diffusive properties of hydrated cement paste. RVE, representative volume element. Reproduced with permission from Stora et al., 2009. © 2009, Elsevier*

porosity along with the crucial role of molecular modelling in this important endeavour (Pellenq *et al.*, 2008).

For example, Jennings's model incorporates the insights gained from neutron and X-ray scattering measurements which reveal the existence of approximately 4 nm sized C–S–H features to propose that C–S–H gel is made up of the aggregation of 4 nm sized C–S–H brick-like blocks (Jennings, 2008; Skinner *et al.*, 2010). According to this model, the C–S–H bricks can aggregate to form high-density C–S–H or low-density C–S–H depending on a packing factor.

A parameter of the solid phase, such as the density, of hydrated Portland cement can be measured on heating to constant weight at 105°C by pycnometric methods using a saturated solution of calcium hydroxide as a fluid. The non-solid phase of cement paste is characterized by porosity, size distribution of pores, specific surface area and hydraulic radius. The first two characteristics are usually determined by means of mercury intrusion porosimetry and based on isotherms of adsorption of water or nitrogen. The mercury porosimetry method uses the fact that the mercury does not moisten a porous solid phase and hence will enter into pores under pressure. The total porosity can be also determined using organic liquids or water. The specific surface of the hardened cement paste is the area accessible to external gases or liquids. The hydraulic radius is the average characteristic of a porous structure defined as the ratio of total porosity to total specific surface.

Table 5.3 *Methods of analysis of the composition and structure of cements*

Methods	Types	Note
Diffractometry	X-ray diffraction (XRD) Synchrotron X-ray powder diffraction Tomographic energy-dispersive diffraction	Quantitative/qualitative phase analysis
Microscopy	Optical microscopy SEM High resolution SEM Transmission electron microscopy (TEM) Environmental SEM	Structure analysis
Thermal analysis	Differential thermal analysis (DTA) Thermogravimetric analysis (TGA) Differential scanning calorimetry (DSC)	Understanding of the complex physico-chemical phenomena associated with the formation and behaviour of cementitious compounds, composition analysis (Ramachandran and Beaudoin, 1999)
Spectroscopy	Infrared spectroscopy (IR) spectroscopy Raman spectroscopy Flight-secondary ion mass spectrometry	Determination of molecular structure, identification of chemical species, quantitative/qualitative determination of chemical species
	Diffuse reflectance Fourier transform infrared DR-FTIR spectroscopy	This technique is used in the investigation of matter in the solid, liquid and gaseous states
	Nuclear magnetic resonance (NMR) spectroscopy Magic-angle spinning (MAS) NMR ^{1}H, ^{27}Al and ^{29}Si MAS NMR $^{1}H(^{15}N, \alpha,\gamma)^{12}C$ Nuclear resonance reaction analysis (NRRA)	Atomic-scale structure and dynamical behaviour (Ramachandran and Beaudoin, 1999)
Scattering	Neutron scattering Quasi-elastic neutron scattering X-ray scattering Low angle X-ray scattering Small angle X-ray scattering	Atomic-scale structure
Other methods	Energy dispersive X-ray analysis Ultrasound attenuation X-ray tomography X-ray fluorescence Wave emission and propagation Selective dissolution ^{1}H NMR relaxometry Wet chemistry	

Other methods such as ultrasound attenuation, acoustic emission detection, adsorption measurements, small angle neutron scattering, X-ray tomography, ^{1}H NMR spectroscopy and thermoporosity have provided supplementary information on the composition and structure of the hardened cement paste, often obtained in combination with mercury intrusion porosimetry (Münch and Holzer, 2008; Spasova and Ojovan, 2008; Promentilla *et al.*, 2009; Sun and Scherer, 2010; McGlinn *et al.*, 2010; Zhou *et al.*, 2010).

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6

Radioactive Waste Cementation

Characteristics and compositions of generated wastes play a key role in the selection of the waste management technologies (Section 1.4) as inappropriate waste characterization will increase the risk of operating the process unsatisfactorily. Radiological, physical and chemical characteristics of the wastes are important factors that affect the selection of treatment and immobilization technology. A list of important physical, chemical and hazardous waste characteristics is illustrated in Table 6.1 [International Atomic Energy Agency (IAEA), 2001; Abdel Rahman *et al.*, 2011]. This chapter will present the characteristics of resulting wastes that are generated from different waste treatment processes and the suitability of cement-based material for immobilizing these wastes with a special reference to the role of additives to enhance the performance of the cementitious wasteform.

6.1 Radioactive Waste Streams for Cementation

Operational and decommissioning activities of different nuclear facilities led to the generation of different radioactive waste streams. The characteristics of these streams greatly affect the selection of cement as a host media to immobilize and stabilize these wastes (IAEA, 1999a). Radioactive wastes are categorized based on their physical state as gaseous, liquid, dry solids, wet solids and decommissioning wastes (major end items); subcategories of these types are listed in Table 6.2 (IAEA, 2001; Abdel Rahman *et al.*, 2011). This section will introduce characteristics of different waste categories generated as a result of decommissioning activities, whereas waste generated during operational phases was introduced in Section 1.2.

Cementitious Materials for Nuclear Waste Immobilization, First Edition. Rehab O. Abdel Rahman,
Ravil Z. Rakhimov, Nailia R. Rakhimova and Michael I. Ojovan.

Table 6.1 *Important waste characteristics*

Physical properties	Chemical properties	Hazardous properties
Physical state	Chemical composition	Infectious hazard (biowastes)
Density	Organic content	Explosive hazard (low flash point)
Morphology	Acidity/alkalinity (pH)	Corrosive hazard
Compaction ability	Chemical stability	Radiological hazard
Level of segregation	Toxicity	—
	Redox potential	—

Table 6.2 *Nuclear waste categorization according to type*

Wet solid wastes	Dry solids	Major end items	Liquid
Spent ion exchange resin	Paper	Steam generators	Oils
Precipitation sludge	Plastic	Core barrels	Scintillation
Evaporator concentrate	Metal	Pressurizers	Solvents
Cartridge filters	Concrete	Heat exchangers	Aqueous
Filter media	Building rubble	Turbines	—

At the end of any nuclear facility operation, it must be decommissioned. Planning for this phase is performed based on clear identification of the radiological and physical characteristics of the facility. Then decommissioning strategy, decontamination and dismantling needs, workers, public and environmental radiological protection requirements are identified (IAEA, 1999b). A well planned waste minimization strategy is typically adopted to reduce the volume of the generated wastes during this phase. To manage the generated waste, onsite waste management facilities might be installed such as a waste segregation unit, cleanup/decontamination processes and waste treatment and cementation units. Depending on the nature of the facility and waste volume and activity level, the resultant waste treatment and immobilization technologies are selected.

Decommissioning of mill facilities involves major activities such as decontamination/cleanup, equipment dismantling, structures demolition, waste reduction to manageable pieces, cementation of reduced radioactive materials, debris transportation to tailings pile and cementitious wastes disposal (IAEA, 1999a, c). Special containers are used to facilitate handling, transportation and cementation of the metal wastes as that was proved to be cost-effective.

Nuclear laboratories and installations generate significant quantities of radioactive wastes during the decommissioning phase. The generated wastes are mainly low level and the contamination extent is dependent on the spectrum of isotopes used in the facility. A list of generated waste streams from the decommissioning activities of different nuclear facilities is as follows (IAEA, 2003a):

- High energy particle accelerators generate waste containing a high volume of low-level solid activation products.
- Linear accelerator decontamination activities are mainly conducted on the collimation heads; the major contaminants include ^{57}Co, ^{60}Co and ^{181}W.

- Depleted uranium shield is managed as radioactive waste.
- Reinforced concrete shield may be contaminated with ^{60}Co, ^{3}H, ^{152}Eu and ^{154}Eu.
- Reactor vessel and system components in research reactors may be activated to high levels requiring remote dismantling. Internal surfaces in a reactor may be contaminated by corrosion products. They may also be contaminated by fission products and long-lived alpha-emitting nuclides if there has been fuel leakage. Beryllium, frequently used to increase the neutron flux in research reactors, poses a special waste problem due to its high chemical toxicity.

The decommissioning wastes of nuclear power plants include gaseous waste that might result from specific air purification needs, such as underwater plasma cutting, wet abrasive and dry cutting techniques which generate aerosols, hydrogen gases and dust. Liquid wastes are also generated in the form of effluent from chemical decontamination units. Several chemical decontamination technologies are used commercially, among them the REDOX or SODP process proved their efficiency for decontaminating complicated equipment shapes, such as valves, pumps and small diameter pipes (Environmental Protection Agency, 2006). The characteristics of major solid waste streams generated during the decommissioning of a pressurized water reactor, as representative for decommissioning wastes, are listed in Table 6.3 and Table 6.4 (Klein *et al*., 2006).

Table 6.3 *Dry solid waste generated from decontamination and dismantling of a pressurized water reactor*

Waste	Characteristics
Protective clothing, wood from ventilated hoods, laboratory furniture	Burnable solid wastes, low level
Bulk metallic wastes from dismantling of reactor internals, reactor pressure vessel, primary pump, reservoir, valves, structure, electric cables, light supports	Compactable and non-compactable, low to high activity level
Bulk concrete waste from slightly activated slabs, floors, shielding walls, room walls	Large volume, low level
Isolation and asbestos	Non-metallic compactable
Contaminated lead bricks	Special category

Table 6.4 *Wet solid wastes from different sources from decommissioning of a pressurized water reactor*

Major wastes	Source	Characteristics
Ion-exchange resins	Cleaning storage well pool and refuelling pool	Medium activity level <100 l/year
	Full decontamination of primary system	Medium–high activity level <100 l/year
Sludge	Deposits in reservoirs and liquid sumps	Low–high activity level
	Cutting by diamond, saw or coring using water as cooling media	
Cartridge filters	Purification of storage pools, and underwater cutting system	Generation range 2–400 l/year
Swarfs, dross, chips	Underwater cutting operations	—

The utilization of mobile waste management units could reduce the decommissioning phase costs. For example, a metal melt system may cost in excess of US$10 million to build and another US$500 000 or more per year to operate and maintain. If the volume of metal waste is on the order of only 50 t per year, the cost of constructing and operating a metal melt system is difficult to justify (IAEA, 2006a). These costs could be reduced by either using regional, centralized, off site processing facilities which accept waste from many nuclear facilities or by using mobile systems which can be transported between multiple nuclear sites for processing campaigns.

6.2 Liquid Waste

6.2.1 Organic Liquid Waste for Cementation

Limited amounts of radioactive organics are found in reactor cooling pump oils and accelerator targets. In research and radioisotope production facilities, labelled organic compounds have typically homogenously distributed radionuclides. Oily wastes, that is lubricating oils, hydraulic fluids and vacuum pump oils, are characterized by their relatively small content of beta- and gamma-emitting radionuclides. Scintillation liquids, for example steroids, lipids, toluene and hexane have radioactivity contents of the order of 350 MBq/m^3 (Abdel Rahman *et al.*, 2011).

The hazard of these wastes is not limited to the radiological one but includes hazards related to their nature as organic matter such as volatility, flammability and toxicity. To manage these wastes safely, a large number of techniques is commercially available that are divided into non-destructive and destructive processes. In non-destructive processes the organic content remains intact and physical changes in the waste properties are targeted to enhance the safety and economics of subsequent management activities, that is immobilization, storage and disposal (IAEA, 2004). Non-destructive methods applicable to organic liquid wastes include, but are not limited to, drying, distillation and absorption. On the other hand, destructive techniques involve chemical change in the waste product (e.g. incineration, pyrolysis, plasma treatment). Table 6.5 presents different treatment processes, their applicability and resultant wastes (IAEA, 1992a, b, 1994, 2001, 2003b, 2004). Note that the resultant waste is mainly the primary radioactive waste resulting from raw waste treatment. The secondary waste is by definition a form and quality of waste that results as a *by-product* from processing of waste and therefore, for example the sludge is not a secondary waste (IAEA, 2003c). Secondary wastes typically include cartridge filters, contaminated equipment, processing chemicals and so on. Resulting wastes include both primary and secondary wastes.

A combined process was developed to destroy the organic phase which involves emulsification, adsorption, sedimentation and electorchemical destruction (Brown *et al.*, 2013). An organic emulsifying agent is added to waste in a high shear mixer to give stable emulsions, which are then mixed with graphitic adsorbent (NyexTM) and fluidized. NyexTM is then allowed to settle under gravitational force to form a bed with two electrodes placed at its sides. By passing an electric current, the organic pollutant is destroyed through anodic oxidation. This method is capable of removing 99% of emulsified oil and 80–90% of residual radioactivity to be transferred to aqueous phase. The resulting wastes can be then cemented.

Table 6.5 *Treatment process for organic liquid wastes and resulting wastes*

Process	Waste	Resulting wastes
Absorption	Lubricant and solvent	Sorbent loaded with organic liquid for cementation
Distillation	Scintillation fluid	Water (to be discharged) discharge. The organic solvent can be reused
Drying and evaporation	Organic solvent	Dried concentrate for cementation
Direct immobilization	Lubricant, solvents and others	Solidified matrixes for storage/disposal
Acid digestion	Hexone, TBP	Sludge, inorganic oxides and/or gases such as sulphur and nitrogen oxides
Incineration	Lubricants and solvents	Ashes for immobilization Off gases for treatment
Electrochemical oxidation-Ag II	EDTA	Carbon dioxide, water and organic species
Biological	Low concentration organic containing aqueous streams	Biogas (non-radioactive, except ^{3}H- and ^{14}C-) and sludge
Wet oxidation process (hydrogen peroxide)	30% TBP in n-dodecane (PUREX wastes) Organic acid decontamination reagents Non-polar materials	Mineralized TBP and n-dodecane separated at the top to be recovered
Alkaline hydrolysis process	Between 6 and 30% TBP in diluents, TBP degradation products such as dibutyl phosphoric acid, DBP, mono-butyl phosphoric acid, H2MBP, and phosphoric acid	Sodium salts of dibutyl phosphoric acid forms in the aqueous phase (to be cemented) Butanol remains in the organic top phase (to be incinerated)
Plasma treatment	Vaporizes organic materials (and other volatiles) and to melt metallic or inorganic constituent	The molten residues (metal and/or slag) Gases for off-treatment

Direct immobilization of oils in cement has also been practiced, knowing that the cementation process has a limited efficiency for the immobilization of organic liquids. To ensure production of a dry and high strength monolithic wasteform, the waste loading should be lowered to about 12 vol% (IAEA, 1992b). Low long-term strength of resulting wasteform is attributed to the immiscibility of organics with water, coating anhydrous cement grains and preventing their access to water (Utton and Godfrey, 2010). To increase the waste loading, the utilization of emulsifiers was suggested. Different oil streams, such as turbine oil, pump oil and tributyl phosphate (TBP)/dodecane solvents, have been solidified in cement. The wasteform includes ordinary Portland Cement (OPC), lime, waste, emulsifier and silicate formation accelerator. To prepare the cementitious paste, an OPC–lime mixture and oil–water emulsion are prepared, the mixture and emulsion are mixed until the batch is homogenous. Finally, the silicate cure accelerator is added and stirring is continued to ensure uniform dispersion of the accelerator (IAEA, 1992b). It should be noted that the waste acceptance criteria for cementitious organic waste include compliance with low waste loading and stability criteria (GarcíaQuirós and Gagner, 2001). Recently a new cement–lime–zeolite–coagulant–emulsifier composition was proposed to increase the waste loading to 30 wt% (Tsinguhua University, 2011).

6.2.2 Aqueous Waste for Cementation

Aqueous waste generation is associated with operational and decommissioning activities of nuclear facilities. The radiological and chemical characteristics of the effluent depend on the conducted operation. The selection of the treatment process is largely dependent on the radiological characteristics. For instance, effluents containing low level very short-lived radionuclides (beta/gamma emitters) are stored for decay then if the activity limit falls below regulatory levels, they can discharge to the environment (IAEA, 1999a). Aqueous waste generated during the operation of nuclear research centres can be contaminated by both long- and short-lived radionuclides. These wastes are generally characterized by the uniformity of the produced waste batches of neutral pH. Wastes generated by radioisotope production laboratories are characterized by two types of waste streams, the first is small volume of high specific activity at chemical concentration stream and the second has a larger volume and low specific activity. The contamination of these waste streams is widely variable depending on the production and purity of the targets. Operational wastes from scientific research laboratories are characterized by their variable radionuclide content and variable volumes (IAEA, 2001). Figure 6.1 summarizes aqueous waste sources and their characteristics.

As indicated in Section 1.4.2, combined treatment methods are typically used for chemically variable waste streams. Table 6.6 presents a summary of treatment process suitability, limitations, features and maturity, and resulting wastes (IAEA, 2001, 2006a; Abdel Rahman *et al.*, 2011). The estimation of the volume of waste resulting from treatment is critical during the planning for the cementation unit. The volume of the radioactive wastes from ion exchange, evaporator, filter and membrane processes can be easily estimated. These wastes are directly transferred to the cementation unit, while sludge resulting from treatment is usually dewatered using suitable dewatering techniques. The management of precipitation sludge, and legacy and reprocessing sludge will be fully discussed in this section.

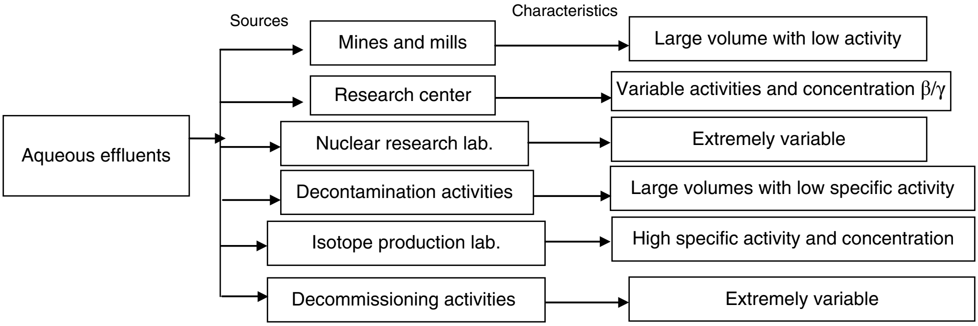

Figure 6.1 *Source and radiological characteristics of aqueous waste streams.*

Table 6.6 *Summary of liquid waste treatment process*

Process	Suitability	Limitation	Features and maturity	Resulting wastes
Precipitation/ neutralization	Large volume	Presence of complexants, trace organics or particulates	Well established in fixed plants	Sludge
	Aqueous liquid		High salt content	
Evaporation	Large volume	Presence of ^{3}H, I and Ru, at high HNO_3 content iron bearing precipitates affect filtration efficiency	Well established in fixed plants	Concentrate
	Aqueous liquid	High capital, energy and maintenance costs, corrosion, scaling or foaming	High salt content and HNO_3	
Ion exchange	Large volume Aqueous liquid	Not suitable for high salt content Blockage problems	Well established in fixed and mobile plants	Exhausted resin
Ion-exchange membrane	Aqueous liquid Solvent	Costly, limited mechanical stability, precipitation affects useful life	Well established in fixed and mobile plants	Exhausted membrane
Reverses osmosis	Aqueous liquid	High pressure system Limited by osmotic pressure Not backwashable Highly susceptible to fouling	Well established in fixed and mobile plants High waste throughput	Exhausted membrane
Membrane filtration	Aqueous liquid	Capacity is limited due to pressure restrictions in system	High removal Long life	Concentrated solids
Incineration	Organic liquid	High temperatures required	Well established in fixed plants	Ashes
	Spent resin	Off-gas filtration and monitoring required	High waste throughput	Spent filters
	Combustible wastes	Activity limit <1000 Bq/g		
Oil filtration	Oils and lubricants	Economical for large volume	Well established in fixed and mobile plants Regenerates oils and lubricants	Filter cartridges
Oil solidification	Oil and oil bearing sludge	*Increased* disposal volume Oil leakage under compressive loading	Well established in fixed and mobile plants	Solid monolith

6.2.2.1 Precipitation Sludge Management

Chemical precipitation is a process that involves the addition of chemicals to alter the physical state of the dissolved and suspended solids and facilitate their removal. Metal hydroxides, carbonates, sulphates and sulphides are added to promote the precipitation process. Different chemical precipitants are commercially available including Alum [$Al_2(SO_4)_3{\cdot}18H_2O$], aluminium chloride ($AlCl_3$), lime [$Ca(OH)_2$], ferric chloride ($FeCl_3$), ferrous sulphate [$Fe_2(SO_4)_3$] and sodium aluminate ($Na_2Al_2O_4$) (Tchobanoglous *et al.*, 2003). The main radionuclide removal mechanisms may include precipitation, co-precipitation, adsorption and ion exchange (Bond, 1980).

Precipitation and co-precipitation are currently applied in many waste treatment facilities to remove potential radioactive contaminant as a pretreatment/treatment method. Oak Ridge National Laboratory, USA uses ferric sulphate to remove Sr and Cs from caustic low-level radioactive wastes (NaOH and Na_2CO_3) (Bostick *et al.*, 1994). Currently TEPCO (Tokyo Electric Power Company) in Japan is testing multi-nuclide removal equipment that is designed to reduce the radioactivity contents below the reactor regulation levels (TEPCO, 2012). The system is composed of three subsystems (A, B, C); the waste will be directed to pretreatment facilities that utilize medical agents, Fe and carbonate co-precipitation and finally an adsorption treatment tower. The Fe co-precipitation treatment facility targets nuclides and organics inhibiting the absorption of radioactive materials, while the carbonate co-precipitation treatment facility targets ^{89}Sr, ^{90}Sr and alkaline-earth metals (Mg, Ca, etc.) that inhibit Sr absorption (Figure 6.2).

The volume of precipitated sludge (V_s) can be calculated by determining the removed solid mass [m_1 = % solid removal × inital concentration (C_0) × flow rate] and the mass of the insoluble products (m_2) calculated from the reaction equations illustrated in Table 6.7. The volume is calculated by dividing ($m_1 + m_2$) by the specific gravity of the sludge and the moisture content.

6.2.2.2 Legacy and Reprocessing Sludge

Sludge in the K basin at the Hanford site, USA is presented as an example of legacy sludge which is composed of degraded fuel, corrosion products, dirt, and other material that has accumulated in the basin over 30years. Sludge is categorized by its location into pit sludge,

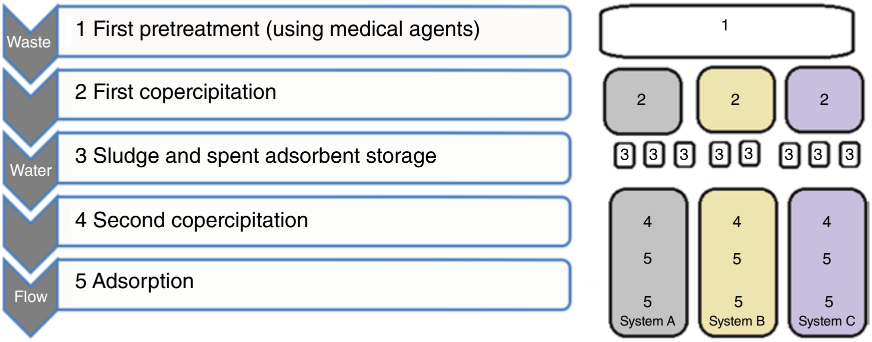

Figure 6.2 *Sequence of treatment process for aqueous liquid waste treatment at TEPCO.*

Table 6.7 *Reaction equation for common precipitant*

Participant	Reaction equation	Main sludge component
Ferric sulphate	$2Fe_2(SO_4)_3 + 3Ca(OH)_2 \leftrightarrow 2Fe(OH)_3 + 3CaSO_4$ Ferric sulphate Calcium hydroxide Ferric hydroxide Calcium chloride	$Fe(OH)_3$
Ferrous sulphate	$FeSO_4 \cdot 7H_2O + Ca(HCO_3)_2 \leftrightarrow Fe(HCO_3)_2 +$ Ferrous sulphate Calcium carbonate Ferrous bicarbonate $CaSO_4 + 7H_2O$ Calcium sulphate Water $Fe(HCO_3)_2 \leftrightarrow Fe(OH)_2 + CO_2$ Ferrous bicarbonate Ferrous hydroxide Carbondioxide $Fe(HCO_3)_2 + 2Ca(OH)_2 \leftrightarrow Fe(OH)_2 +$ Ferrous bicarbonate Calcium hydroxide Ferrous hydroxide $2CaCO_3 + 2H_2O$ Calcium carbonate Water Ferrous hydroxide can be oxidized to ferric hydroxide, the final foom desired, by oxygen dissolved in the waste water $Fe(OH)_2 + \frac{1}{4}O_2 + \frac{1}{2}H_2O \leftrightarrow Fe(OH)_3$ Ferrous hydroxide Oxygen Water Ferric hydroxide	$Fe(OH)_3$
Ferric chloride	$2FeCl_3 + 3Ca(OH)_2 \leftrightarrow 2Fe(OH)_3 + 3CaCl_2$ Ferrous chloride Calcium hydroxide Ferric hydroxide Calcium chloride	$Fe(OH)_3$

(*continued*)

Table 6.7 (*continued*)

Participant	Reaction equation	Main sludge component
Ferric chloride	$2FeCl_3 + 3Ca(HCO_3)_2 \leftrightarrow 2Fe(OH)_3 + 3CaCl_3 + 6CO_2$ Ferrous chloride Calcium bicarbonate Ferric hydroxide Calcium chloride Carbon dioxide	$Fe(OH)_3$
Alum	$3Ca(HCO_3)_2 + Al_2(SO_4)_3 \cdot 18H_2O \leftrightarrow 2Al(OH)_3 +$ Calcium bicarbonate Aluminium sulphate Aluminium hydroxide $3CaSO_4 + 6CO_2 + 18H_2O$ Calcium sulphate Carbon dioxide Water	—
Calcium bicarbonate	$Ca(HCO_3)_2 + Ca(OH)_2 \leftrightarrow 2CaCO_3 + 2H_2O$ Calcium bicarbonate Caclium hydroxide Calcium carbonate Water	$CaCO_3$
Lime	$H_2CO_3 + Ca(OH)_2 \leftrightarrow CaCO_3 + 2H_2O$ Carbonic acid Calcium hydroxide Calcium carbonate Water	$CaCO_3$

Table 6.8 *K-basin sludge characteristics (Pacific Northwest National Laboratory, 2004)*

Sludge	Content	Representative sludge sample	Nominal sludge (m^3)	Decay heat (W/m^3)	U metal (g/cm^3)
Pit	100 nCi/g Pu	Fuel piece	—	—	—
Floor	100 nCi/g Pu	KE	3.64 33.8 6.3	22.4	0.023
Canister	5% U metal content	KE	2.5 2.83 1.01	77 256	0.125 0.2
Knockout pot	>50% U metal content	Fuel piece	0.423	1100	9.4
Settler	100 nCi/g Pu	—	—	—	—

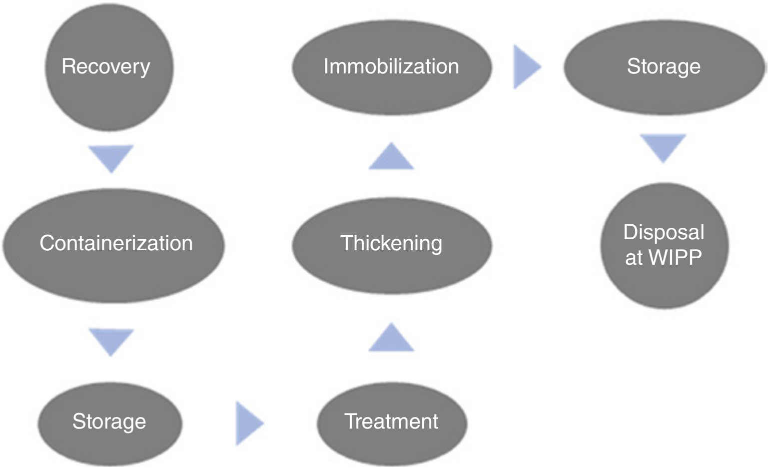

Figure 6.3 *Management scheme for K-basin sludge. WIPP, Waste Isolation Pilot Plant. Developed based on Pacific Northwest National Laboratory, 2004*

floor sludge, canister sludge, knockout pot (KOP) sludge and settler tank sludge. Pit sludge is sub-categorized in accordance with its resident pit (Pacific Northwest National Laboratory, 2004). Spent fuel in the K basin is characterized by its large pieces (>6350 μm), while sludge in the K-east and K-west basins forms 20% of the sludge volume and is characterized by its low dose and uranium content. On the other hand, KOP sludge is highly radioactive and contains large uranium metal pieces (500–6350 μm). Table 6.8 shows the characteristics of different sludge in the K basin.

The spent fuel pieces are planned to be loaded into multi-canister overpack then dried in the cold vacuum drying facility and finally stored in the canister storage building pending disposal. Sludge management includes recovery, immobilization, containerization and shipping to the transuranic disposal Waste Isolation Pilot Plant (WIPP). The detailed description of the management scheme is illustrated in Figure 6.3.

The immobilization of the sludge will be performed using the mobile sludge solidification (MOSS) unit (described in Chapter 7) by mixing it with cement to produce a mixture containing 30% volume sludge. If a sufficiently low uranium metal–water reaction rate cannot be achieved, then an effective means of eliminating the uranium metal from the sludge is required for cementation to be a viable option.

Pulp wastes are legacy wastes accumulated in the Mining Chemical Combine in Siberia, Russian Federation. The pulp is a multi-component waste with significant content of long-lived alpha-radionuclides. The main components in the pulp are Fe_2O_3, Fe_3O_4, AlO(OH), Cr_2O_3, MnO_2, SiO_2, Ni, Sr and Cs (as hydro aluminium silicates), PuO_2 (as silicates, aluminates and aluminium silicates) and U (as polyuranates). As a part of the decommissioning works, pulps will be treated and cemented. The pulp treatment includes removal, dissolution of removed pulp, extraction of uranium and plutonium and collection of undissolved pulp (Sukhanov *et al.*, 2013).

6.3 Bulk Solid Radioactive Wastes

Bulk solid wastes are generated during the decommissioning and dismantling of nuclear facilities. The generated wastes are classified into three main categories:

1. Non-contaminated materials that can be released from regulatory control without any decontamination, for example materials outside the controlled area.
2. Contaminated bulk solids that are technically and economically feasible to be decontaminated below the radiological regulatory criteria. These wastes can be subsequently recycled in the nuclear industry, for example contaminated pumps and pipes.
3. Contaminated bulk solids that cannot be technically or economically decontaminated below the radiological regulatory criteria, such as highly activated concrete.

This section is focused on the management of the second and third categories, where the wastes are classified into bulk metallic, concrete and hazardous wastes.

6.3.1 Bulk Metallic Wastes

Steam generators, pressure vessels, fuel channels and evaporators are examples of bulk metallic solid wastes generated during the decommissioning of nuclear power plants (NPPs). Usually the NPP site includes more than one nuclear reactor, and typically not all the reactors will be decommissioned at the same time. Depending on the amount of contamination, the decommissioning plan and resources, a decision is made to segment and decontaminate these wastes or store them till site decommissioning. If storage is selected, the wastes should be kept dry and sealed to avoid corrosion.

In a NPP that utilizes light water as a primary coolant, the steam generator is typically contaminated by fission product oxides and activated corrosion deposition from the primary coolant on the inner surfaces of the steam generator tubes (primary side). Leakages in the tubes may result in contamination on the outer surfaces (secondary side). The extent of contamination will depend largely on the amount of released materials from the fuel during operation (e.g. via pinhole leaks in the fuel cladding) and on the efficiency of the reactor coolant cleanup system. The total radioactivity in a steam generator is typically in the range

Figure 6.4 *Steam generator storage facility. Reproduced with permission from Nuclear Waste Management Division, Ontario Power Generation Inc., 2009. © 2009, Ontario Power Generation Inc.*

of 1–3 TBq per steam generator, or about 2–5 GBq/t. The steam generators are expected to be classified as low-level waste (Nuclear Waste Management Division, Ontario Power Generation Inc., 2009). Before storage, the steam generator is drained, dried, sealed up and suitable corrosion protection to the sealed surfaces is applied. Figure 6.4 shows a steam generator storage facility at the Western Waste Management Facility at the Darlington Nuclear Generating Site in Ontario, Canada.

After segmentation, a suitable decontamination technique is selected. There are different commercial decontamination techniques that could be used for bulk solids. These techniques include washing, wet mechanical and chemical decontamination. Table 6.9 presents a comparison of different decontamination agents, their scientific basis, target contaminants, treatment and wastes generated on decontamination. As shown in this table, the wastes are generated either as exhausted ion exchangers and/or precipitation sludge. A phosphoric acid decontamination plant is an example of a commercial decontamination plant for metallic wastes. Within this plant, washing, electropolishing and chemical decontamination techniques are available (Klein *et al.*, 2006). The plant is composed of two main parts: the first for the decontamination unit; and the second for the recovery of phosphoric acid. Metallic decontamination is performed in a four-step process. The process includes degreasing the metallic parts, washing, acid cleaning and washing again. Stainless steel is decontaminated using electropolishing, while carbon steel is chemically decontaminated. The dismantled parts are transferred within the plant using a bridge crane fixed above different parts of the plant (Paratore, 2011). The wastes produced from the chemical decontamination process are treated using oxalic acid to produce iron oxalate which is subsequently converted into iron oxide by thermolysis. The iron oxide is then sent to an immobilization plant.

It is worth mentioning that within the nuclear industry, decontaminated metallic wastes can be recycled by melting for the fabrication of shield blocks or waste containers. The recycled material must comply with composition and radiochemical regulatory criteria (Klein *et al.*, 2006).

Table 6.9 *Waste arising from different chemical decontamination methods*

Method	Basis	Target contaminants	Treatment of decontaminant agent	Resulting wastes
Chelating and organic acids	Contaminants binding on organic chemical so that metals are 'enveloped' and changed from its insoluble to soluble state	Fixed contamination	Regenerated by ion exchange Destroyed using oxidant	Exhausted ion exchangers CO_2 and contaminated precipitate
Mineral acids	Hydrogen ions provide by the acid attack the oxides and destabilize the oxide lattice	Variety of contaminant dependent on the acid contaminant interaction	Regenerated by washing	Exhausted ion exchangers or precipitate sludge
	Hydrogen attack the metal surface directly thus releasing bound contaminants		Neutralization	
Chemical foams	Used as carrier media for other chemical decontamination agents	Loose contaminants	Foam dried then rinsed off or removed as a foam	Contaminated swabs
Gels		Particulates and corrosion deposits	Gel is removed by swabs	
Oxidizing and reducing agents	Increase the oxidation state of the contaminant to increase its solubility	Corrosion cruds in metal components	Dissolved contaminants are removed by ion exchangers	Exhausted ion exchangers

6.3.2 Bulk Concrete Wastes

Radiation shielding, contaminated floors, walls and ceiling in different nuclear installations are the major sources of the huge amount of potentially contaminated concrete generated during the decommissioning of the facility. Managing contaminated concrete is a multistep process that is started during the planning phases of the decommissioning project. The selection of the dismantling and decontamination technique can greatly affect the total amount of contaminated materials that will be managed as a radioactive waste. The first step in managing contaminated concrete is to apply a suitable surface removal technique to remove the contamination and then demolition will be performed. Physical decontamination is the best choice for porous surfaces such as concrete on which no barrier layer was placed and where contamination has reached deep within the matrix. In such situations, a chemical approach is rarely successful and may worsen the situation by driving the contamination even deeper below the surface. Table 6.10

Table 6.10 *Waste arising from different physical decontamination methods*

Method	Basis	Applicable media	Resulting wastes
Strippable coatings	The coatings penetrate into microvoids on the surface and adhere to the contaminants, allowed to set or cure and then removed with the coating	Bare and painted concrete, wood, carbon and stainless steel, plastic and insulation	Cured, stripped coating Minor amounts of waste water
Centrifugal shot blasting	Hardened steel shot is propelled at contaminated surfaces to fracture the surface	Bare, painted and coated concrete surfaces	Dusty mixture of paint chips and concrete, spent shot. Personal protective equipment, HEPA filters
Concrete grinder	Diamond grinding wheel is used to decontaminate and strip concrete surfaces	Interior and exterior flat or slightly curved concrete surfaces	Personal protective equipment, plastic wrapping and sleeving for vacuum hoses and the concrete dust collected by the vacuum
Concrete shaver	Electrically driven, self-propelled system	Large, flat, wide-open surfaces	Dusty mixture of paint chips and shaved concrete. Personal protective equipment, HEPA filters
Dry ice blasting	Uses carbon dioxide pellets (>3 mm) as the blasting medium. The pellets are accelerated by compressed air with pressures in a machine then targeted at the contaminated surface	Cement, concrete, plastic, wood, stainless steel and other metals	HEPA filter and particles removed from the surface
Electro hydraulic scabbling	Uses a short high current high discharge between two electrodes in water to create a plasma bubble and a shockwave capable of scabbling concrete surfaces	Flat concrete surfaces	Scabbling debris and process water

(*continued*)

Table 6.10 (continued)

Method	Basis	Applicable media	Resulting wastes
En-vac robotic wall scabbler	Remote-controlled grit blasting unit; consists of the En-vac robot (the unit that performs the scabbling), a recycling unit, a filter and a vacuum unit	Flat-surfaced painted walls and floors and carbon steel surfaces	Scabbled concrete and paint debris containing small amounts of recyclable grit
High pressure water	By flushing with water, soluble contaminants are dissolved and unbound particulates are dislodged and carried away. Increased pressures and flow-rates enhance the mechanical effects of the water stream	Concrete, brick, tile, metal and similar material, porous and non-porous surfaces of simple and complex geometric structures	Waste water containing particulates and debris removed from the surface and abrasive media

HEPA, high-efficiency particulate air.

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lists different applicable physical decontamination techniques and the nature of the arising resulting wastes.

6.3.3 Bulk Graphite

Graphite is used in reactors as a neutron moderator and reflector, a structural material and a fuel-element matrix material. It has been deployed in about 250 uranium (or UO_2)-graphite reactors such as the UK's Magnox and advanced gas cooled reactors, the French uranium natural graphite gas, a small number of high-temperature reactors, the Soviet-era graphite moderated light water cooled reactors and in numerous 'production' reactors and materials-testing reactors. Most of those reactors are now quite old, with many already shutdown. During reactor operation, graphite is exposed to high integral neutron flux so radioactivity arises from the activation of impurities initially present in it and activity transported from other parts of the reactor circuit. On decommissioning of the reactor, irradiated graphite waste is generated; the global inventory currently is assessed as about 260 000 t (IAEA, 2006b; Ojovan and Wickham, 2014). Cementation remains the favoured technical option for irradiated graphite waste although cements can be used simply to grout the graphite blocks or the graphite waste can be crushed and used in combination with cements to immobilize other solid radioactive waste in containers (Ojovan and Wickham, 2014).

6.3.4 Bulk Hazardous Wastes

Hazardous materials are major factors for consideration in the decommissioning of old nuclear facilities and can represent a risk both to the operators undertaking the work and to the environment in general. Examples of common hazardous materials are asbestos, polychlorinated biphenyls, lead, mercury and beryllium. All these materials, depending on the national policy in the particular country, require a special approach, even if they pose no radiation hazard. Asbestos is unexpectedly ubiquitous in interior and exterior wallboard, spackling and grouting material, and floor coverings in different old NPPs. Three types of asbestos-containing materials were utilized in old NPPs. The first type was sprayed on surfaces as decorative material, used on the underside of concrete slabs or docking or as fireproofing materials on structural members. The second type was used as thermal system insulation that was applied to pipes, boilers, tanks and ducts to prevent heat loss or gain or condensation. The third type consisted of miscellaneous asbestos-containing ceiling or floor tiles, textiles and asbestos-cement panels, asbestos siding, transit panels and roofing materials (Interstate Technology and Regulatory Council, 2008). For worker safety, asbestos-containing materials are removed prior to demolition activities after radiological decontamination. The removed asbestos is bagged and disposed of in industrial disposal while radiological contaminated asbestos is shipped for treatment.

Lead is used as a shield in the form of lead brick, apron, tray and containers. The extent of lead contamination is limited, so mostly lead is recycled via melting. A melting campaign of lead material contained inside a metallic structure was cited in the BR-3 controlled area at SCK·CEa in Belgium. This was done by placing a heating mattress around the metallic structure and applying heat. Once the lead is melted, a tap welded at the end of the structure is opened to run the molten lead into the ingots. As the melting point of the metal structure is higher than that of lead, the structure does not melt during this process (IAEA, 2008).

6.4 Fragmented (Dispersed) Solid Wastes

Fragmented solid wastes are produced in the form of tailings during nuclear material mining, and during the operation and decommissioning of different nuclear facilities. The common practice for managing dispersed tailings is to neutralize them prior to disposal. The effect of adding neutralizing agents has to be investigated carefully; adding carbonate compounds might increase uranium solubility due to the formation of highly mobile uranyl-carbonate complexes. Circumneutral to slightly alkaline pH values can reduce the uranium solubility. Another method employs the addition of buffering capacity to reduce the potential for acid generation within the tailings mass and, hence, the potential source for contaminants. The choice and quantity of neutralization agents needs to match the predicted long-term conditions within the tailings deposit as well as the conditions at the time of disposal (IAEA, 1999a, b, c).

Tailings can be mixed with suitable binder to produce a consolidated material. Binders such as cement have a triple effect on the tailings properties: a chemical bond is created between constituent particles, some of the pore water is consumed and the pH is raised. Using residues or waste products with suitable hydraulic properties, such as fly ash, may be of economic advantage. For instance, it is common practice in underground base metal mining to prepare tailings into a cementiferous paste suitable for return to underground workings to stabilize stops so that adjacent ore blocks may be removed. In the uranium mining industry this technique formed part of the Australasian Jabiluka mine proposal. The proposal was to return 75% of the tailings to the underground workings as cementitious paste. The remainder was to be placed in either purpose-built pits or underground stopes in benign rock. The potential for groundwater contamination from this underground disposal of cemented tailings was given special scrutiny in the environmental impact assessment process (IAEA, 1999c). To be suitable for the application of paste technology, tailings should contain at least 15 wt% of particles less than 20 μm in diameter to avoid segregation. At Jabiluka, the tailings have more than 30 wt% of this particle size range.

Tailings slurry or pastes are mixed with inorganic binder that promotes both physical and chemical stability of the tailing. The most widely used binder is Portland cement because of its availability and ease of handling, low technology requirements, relatively low cost and well understood cementing and neutralizing capacity. Mixing ratios of cement to waste, and water content, can significantly affect strength, leaching resistance and cost of application. Optimal ratios for use of cement as a binder in low-level mixed waste is found to be 0.5–2.0 kg (cement)/kg (waste) and 0.3–0.33 kg (water)/kg (waste), however these ratios are prohibitive for treatment of the large volumes of tailings.

Fragmented solid wastes from the operation and decommissioning of nuclear facilities are divided into several main groups (compactable, combustible and non-compactable, non-combustible) to facilitate their treatment. The largest volume of fragmented solid waste includes protective clothing, plastic sheets and bags, rubber gloves, mats, shoe covers, paper wipes, rags, towels, metal and glass. Based on the activity level at very short half-life (<100 day) of these wastes, they can be disposed of with municipal refuse after decay storage. Otherwise these wastes are treated to reduce their volume (when compactable, combustible) then immobilized in a suitable matrix.

6.4.1 Compactable, Combustible Wastes

Most of the generated solid wastes during the operation of any nuclear facility are compressible or combustible materials. There are different commercial technologies to deal with these wastes that include compaction, direct immobilization, incineration, pyrolysis, plasma treatment and molten salt oxidation (Ojovan and Lee, 2005). Compaction is a physical treatment process that involves compressing solid waste to reduce the volume. Different types and designs of relatively simple compactors with compressive forces between 100 kN and 50 MN are available offering varying volume reduction possibilities. Compactors are classified according to the applied compressive force as low and high force compactors. This technique is effective for most solid organic wastes; dry active waste (paper, plastic, etc.), light metallic wastes and air filters, where incineration ashes, ion-exchange resins, wood concrete, air and liquid filters are compacted in a high force compactor (Garamszeghy, 2011). The resulting wastes are in the form of compacted solid pellets to be sent for immobilization; the associated airborne radionuclides should be filtered and any liquid found should be treated. Different classes of compactors are widely used worldwide, namely in-drum compactors and drum crushers.

Incineration is a proven thermal method for reducing the volume of organic wastes, both solid and liquid. Incineration involves oxidation of burnable components of the waste; the end products of this process are inorganic ash residues and vapours, aerosols and gases.

Table 6.11 *Combustion processes applied to organic radioactive wastes*

Techniques	Process	Resulting wastes
Incineration	Allow an excess or limited oxygen supply during the primary combustion process	Ashes to be immobilized, for example cemented. Off gas to be filtered
Pyrolysis	Restricting the air supply, pyrolysis of organic materials causes their thermal degradation and a distillation of the volatile fraction, forming combustible liquids and vapours	The material remaining after pyrolysis is char, a charcoal-like substance consisting primarily of fixed carbon residue. Off gas to be filtered
High temperature slagging	Burn the carbonaceous residue by receiving heat	Glass-like aggregate. Off gas to be filtered
Fluidized bed	Inert bed of particles kept in suspension by fluidizing air flowing through the bed at a rate that is just rapid enough to sustain that condition	Solid residues in the form of fly ash suitable for cementation. Off gas to be filtered

Reproduced from Abdel Rahman and Zaki, 2009. With permission from Elsevier.

There is a diverse range of combustion technological options available; Table 6.11 presents a comparison of the different combustion technologies (Abdel Rahman and Zaki, 2009). The selection of an appropriate technology is bound by administrative factors and the preferred volume reduction, low operating costs and the capability to process a variety of non-homogeneous wastes (IAEA, 1986, 1987, 1992a). Incineration results in wastes in the form of exhausted filters and inorganic dispersive residues that can have enhanced specific toxicity. These wastes are directed to immobilization by cementation, super-compaction or vitrification (Ojovan and Lee, 2011).

6.4.2 Non-compactable, Non-combustible Wastes

Fragmented non-compactable, non-combustible solid wastes include ion-exchange resin, cartridge filters and membranes. These wastes are produced from the treatment of primary waste streams. Ion-exchange resins are classified into organic and inorganic resins. Organic ion exchangers are used to filter and purify spent fuel pond water. These exchangers have functional groups that electrostatically host ions to be exchanged with contaminant in pond water. Depending on the type of the functional group, ion exchangers can be divided into: strongly acidic (i.e. $-SO_3H$), strongly basic (i.e. $=N^+$), weakly acidic (i.e $-OH$) and weakly basic (i.e. $-NH_2$). Polystyrene divinylbenzene resins can act as cation exchangers by sulphonation (addition of $-SO_3H$ functional group, where H^+ is the counter ion) or as anion exchangers by adding a $-NH_3^+$ or $-N_2^+$ functional groups, with OH^-, Cl^- or other anions as the counter ion. Phenolic resins, phenol-formaldehyde condensation products, are very weak acid exchangers. Sulphonation of the phenol prior to polymerization can be used to increase the acid strength. Acrylic resins are weak acid ion-exchange resins, with weakly ionized carboxylic acid groups. Under neutral conditions the $-COOH$ functional groups have very little capability for separating the cations from a salt (Ojovan and Lee, 2005).

Table 6.12 *Utilization of inorganic ion exchangers in the UK nuclear programme*

Inorganic exchanger	Utilization
Clinoptilolite (natural zeolites)	SIXEP, Sellafield, to remove caesium and strontium, which are the main contaminants in effluent from fuel storage ponds
AW500 synthetic aluminosilicate zeolite	Remove caesium from fuel storage pond water on Magnox sites
Decalso Y and other inorganic ion exchanger	Magnox station storage ponds

Inorganic ion-exchange materials are used to remove radionuclides from spent fuel pond water or other solutions generated during reprocessing, decontaminate different aqueous streams and treat the primary waste streams. A variety of synthetic and natural ion-exchange materials are used. Examples of inorganic ionic exchangers utilized within the nuclear programme in the UK are illustrated in Table 6.12 (Utton and Godfrey, 2010).

Spent ion exchangers can be regenerated for future use or treated as radioactive waste. Regeneration of organic resins results in the production of highly acidic and caustic radioactive liquids. Hence, the preferred option is direct immobilization. Direct immobilization of exhausted ion exchangers in cement is characterized by its low loading, where only up to 20% wet resins to the dry blend of solidification agents can be used. Increasing the waste loading can lead to swelling and cracking of the produced wasteform. Recently the optimization of cement–ion exchanger waste matrixes has received considerable attention to increase waste loading and enhance the mechanical and contaminant performance of these matrixes.

Research has indicated that suitable chemical decomposition, acid digestion, and incineration could be used to reduce the volume of organic exchangers. Another way to reduce the volume of resins, polymer and chlorine-containing (e.g. PVC) wastes and biological objects is the utilization of thermo-chemical decomposition. The wastes are incinerated using powder metal fuels whose composition is designed (taking account of the waste's chemical composition) to provide simultaneously both complete decomposition of organic matter in the waste and to confine hazardous radioactive and chemical species in the ash-slag residue (Ojovan and Lee, 2005). During the 1980s, wet oxidation of organic ion-exchange resins received great attention to reduce the volume of these exchangers (Hawkings *et al.*, 1980; Lee, 1981; Ichihashi *et al.*, 1984; Ghattas and Eskander, 1987; Wilks *et al.*, 1991). One method relies on transformation of insoluble organic resin to soluble fragments where hydroxyl radical attack causes fragmentation cleavage of benzyl ring systems and alkyl cross-linkages (Fenton, 1894; Twissel and Holt, 1996). The new resin fragments continue their oxidation in solution, ultimately almost all the original organic carbon structure will be converted to carbon dioxide, water and inorganic salts residues. Figure 6.5 illustrates the mass balance of the materials used in wet oxidation of organic resins. The residues can be immobilized in a cementitious matrix. A mixture of blast furnace slag (BFS) and OPC in a 9 : 1 ratio by mass, and 17% dry residue was found to be the most appropriate. It was found that the utilization of wet oxidation prior to conditioning in cement can reduce the volume of the waste by 66% (Twissel and Holt, 1996).

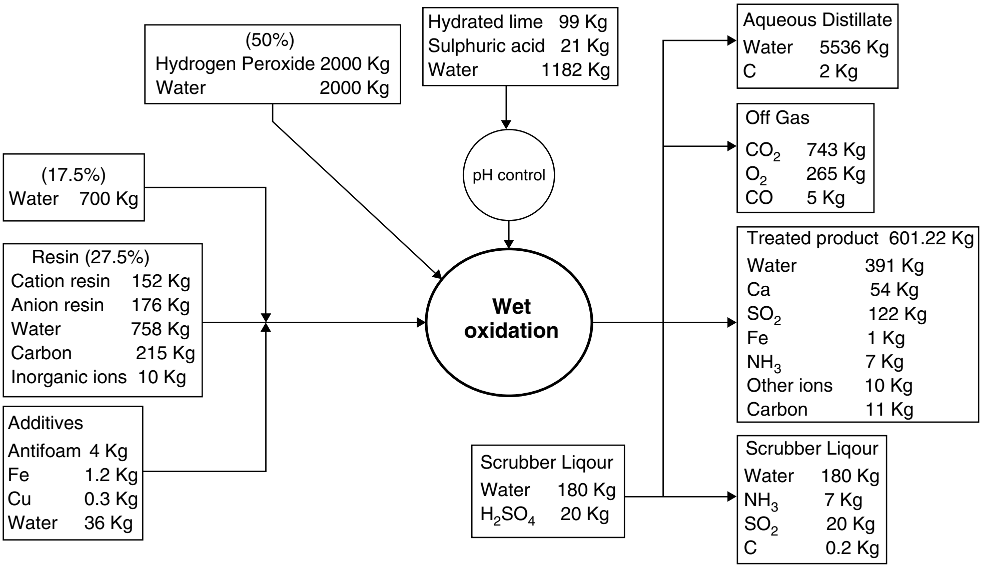

Figure 6.5 *Mass flow sheet through spent organic resin treatment using wet oxidation. Reproduced with permission from Twissel and Holt, 1996. © 1996, Publications Office of the European Union*

Sealed radioactive sources are classified as non-compactable, non-combustible wastes; if not returned to the supplier, they are conditioned to produce a stable waste package that complies with transport regulations, requirements for long-term storage and/or waste acceptance criteria for disposal. Conditioning is usually conducted by embedding the source in a concrete, metallic alloy or via encapsulation in stainless steel.

6.5 Additives for Radioactive Waste Cementation

In many applications a portion of cement (typically OPC) is substituted by a supplementary material, for example fly ash or slag. The aim of using these materials is to either enhance containment and/or mechanical performance of the produced waste form. Additives could be used to improve the workability of the cement paste by reducing grout viscosity and accelerate or retard setting. To achieve the best wasteform performance, a number of factors could be varied during matrix optimization that include, but are not limited to, waste chemical, physical and radiological characteristics, cement type, water/ cement ratio, waste loading percentage, additives properties and percentage, mixing order and emplacement and curing (Drace *et al.*, 2012). The enhancement of containment performance relies on using additives that can activate a retention mechanism and reduces the contaminant release from the wasteform. These mechanisms can enhance contaminant sorption and/or precipitation by affecting radionuclides speciation that change their state to less or more soluble. Table 6.13 illustrates the different types of additives and their action mechanisms for various problematic elements. In this section different potential additives and their effects will be reviewed.

Table 6.13 *Additive types for cementation of problematic contaminants*

Problematic contaminant	Mechanism	Additive type
Amphoteric elements	Control and buffer pH	Lime, acids, fly ash, kiln dust, calcium carbonate, sodium carbonate, soda ash and magnesium oxide
Amphoteric elements	Speciate, precipitate, respeciate	Sulphur and organo-sulphur compounds; soluble silicates and rice hull ash; carbonates; phosphates (especially important for lead) and trisodium phosphate; $FeSO_4$
Metals, non-metals, organics and organometallic compounds	Oxidation reduction	Ferrous sulphate, sodium bisulphite and sodium metabisulphite, ground granulated BFS
Neutral, complexed or organometallic compounds	Sorption and ion exchange	Fly ash, rice hull ash, clays

Generally, cement has acceptable mechanical performance, however mixing the waste stream with cement, especially at high loading rates, can negatively affect this performance. Additives such as BFS, rice husk, some clays and fly ash are used in this respect to enhance wasteform performance. The additives enhance the mechanical performance by changing the permeability, compressive strength, durability and reduce the hydration heat (Escalante-Garcia and Sharp, 2001). If the additives have pozzolanic effect, they will react with the Portlandite (CH) phase to produce additional calcium silicate hydrate phases. This reaction is slow compared with that of the Portland cement, leading to a lower strength at early ages and similar or higher values at later ages (Carrasco *et al.*, 2005; Abdel Rahman *et al.*, 2013). The utilization of ground granulated BFS to immobilize phosphate effluent produced from the reprocessing plant indicated that the compressive strengths of produce waste matrix exceeded 10 MPa after 28 days curing at a waste loading greater than 13 wt% (Sugaya *et al.*, 2009). Addition of 90% ground granulated BFS to 10% OPC was used to immobilize medium-level radioactive waste; studies indicate that the produced wasteform has an improved mechanical performance (Connell, 2008).

6.5.1 Lime

The water solubility of the majority of metals shows a decreasing pattern with increasing pH. Amphoteric elements are characterized by their high solubility in both acidic and alkaline conditions. These elements are soluble in the high pH environment of cement, so to reduce their solubility, the cement pH needs to be adjusted. Buffer materials may be used as additive to control the pH in a range at which these elements have minimum solubility. Lime is used in this respect to control pH and to supply additional calcium for reaction and react with certain interfering organics (Hoeffner *et al.*, 2005). Slaked lime was used as additive to produce Masonry cement. In the presence of water, the extremely high alkalinity induced by the slaked lime induces a rapid set. Masonry cement is particularly useful for solidifying wastes such as boric acid and borate salts, bead resins and filter sludges, which tend to inhibit or retard hydration of other cements (Ojovan and Lee, 2005).

6.5.2 Blast Furnace Slag

Adding a reducing agent to the cementitious matrix has been used to improve the containment and performance of the produced wasteform. The utilization of BFS as additive is not only supported by its effect as a reducing agent but also due to its ability to decrease the pH in pore water, precipitate sulphides and reduce the permeability of the matrix (Shi, 2005). The reduced permeability yielded from the low permeability of the slag contributes to the lower diffusion rate of ions through the hardened cement and improves durability in the presence of salts such as chloride and sulphate (Ojovan and Lee, 2005). BFS has been investigated for its usage as additive for phosphate effluent from a reprocessing plant, borate radioactive liquid waste and alkaline salt solution (Abdel Rahman and Ojovan, 2014). Using a ternary system of OPC–BFS–fly ash was tested for the immobilization of alkaline salt solution. The main mechanisms to enhance the containment performance of chromium, technetium and nitrate were due to permeability reduction, chromium and technetium reduction and precipitation of reduced ions (Langton, 1989; Shi, 2005). The ternary system has been also tested to immobilize the ion exchanger Cs-Ionsiv, with a small fraction (≤1.6 wt%) of Cs inventory released from the encapsulated Ionsiv during leaching experiments (Jenni and Hyatt, 2010). The same ternary system was used effectively to immobilize waste containing high sulphate stream (Ojovan and Lee, 2005).

6.5.3 Clay Minerals

Clay minerals are used effectively as an additive to immobilize organic wastes and streams of high alkali metal contents. This effectiveness is related to the charged structure of the clay that hosts metal ions in its structure. Organic wastes are retained on clay due to a substitution reaction between the quaternary ammonium compounds and the metal ions. This substitution leads to increase in the inter-planar distance between aluminium and silica allowing the clay to sorb more organic compound (Gibbons and Soundararajan, 1989). The containment of alkali metals on clay minerals is also attributed to the cation substitution on clay structure. The cation exchange capacity (CEC) is an important property in assessing the sorptive behaviour of any material as sorption occurs on the exterior surface of the sorbent, so the higher surface area indicates that there are more available sites for radionuclide containment (Abdel Rahman *et al.*, 2012). The presence of narrow channels in the molecular structure of clays might be attributed to the physical entrapment of contaminant in the material structure (Abdel Rahman and Ojovan, 2014). Bentonite, vermiculite and illite, are common clay additives used in the immobilization of different waste streams. It is worth noting that the presence of competing ions in the waste stream can affect the performance of the additives, higher salt concentrations of sodium or calcium can suppress the clay selectivity for caesium and strontium. At low salt concentrations, caesium distribution ratios were high for natural and synthetic aluminosilicates. Vermiculite, clinoptilolite, other synthetic zeolites, phosphates, ferrocyanides and carbon adsorbents showed relatively low selectivity for strontium (Hoeffner *et al.*, 2005).

Bentonite is mainly composed of montmorillonite that has a superimposed tetrahedral–octahedral lattice. Within this lattice, aluminium, iron or magnesium is surrounded by oxygen and hydroxyls in an octahedral configuration that is linked to the silicate

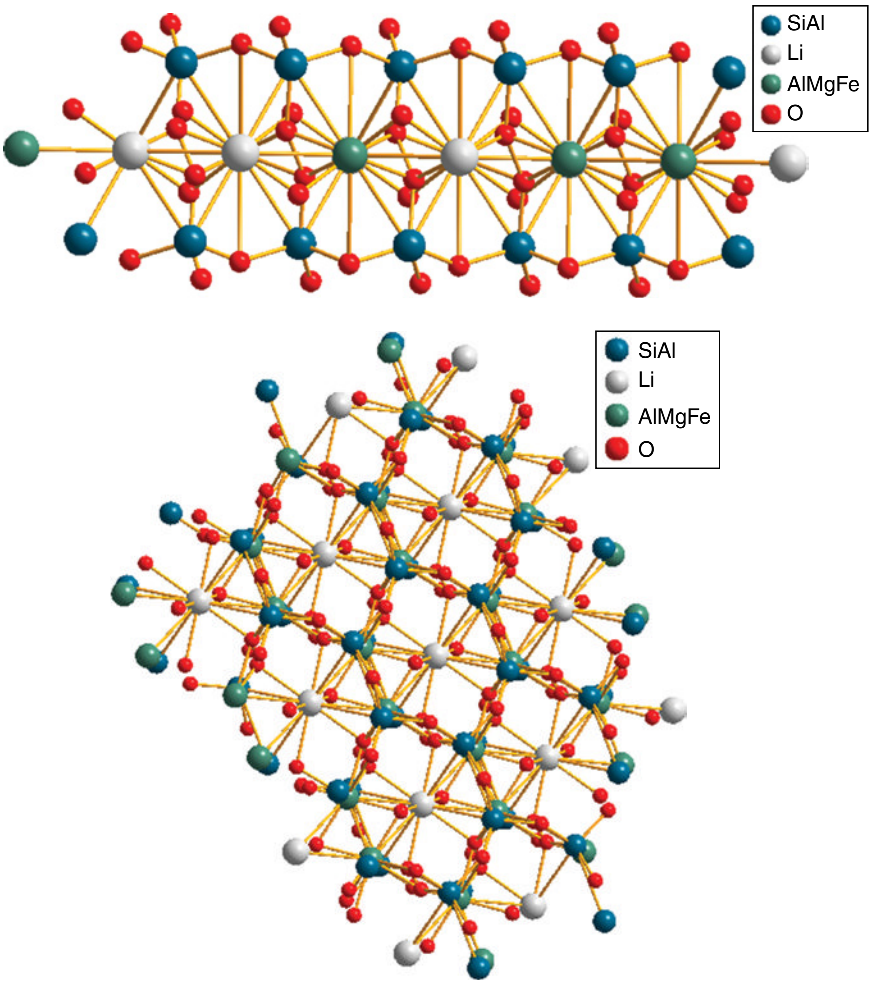

Figure 6.6 *Molecular structure of montmorillonite*

tetrahedra. Two different projections of the molecular structure of montmorillonite are illustrated in Figure 6.6. The montmorillonite lattice, as for any clay mineral, is negatively charged owing primarily to the amorphous replacement of ions within the structure (Abdel Rahman *et al.*, 2013). About 10% of the charge on the surface of bentonite is caused by the protonation and deprotonation of the edge sites (Muurinen, 2011). This negative charge is balanced by the hosted cations which are held on the surface of the flakes; alkali metal can exchange with these cations. Cement–benonite wasteforms were found efficient in reducing the release of alkali metals from sludge and evaporator concentrates (Plecas, 2005; Plecas and Dimovic, 2006; Plecas *et al.*, 2006; Abdel Rahman *et al.*, 2007, 2013; Muurinen 2011).

Vermiculite has a trioctahedral 2:1 layer and an interlayer containing both Mg^{2+} and Al^{3+}, which are able to hold two water molecules in the interlayer. The molecular structure

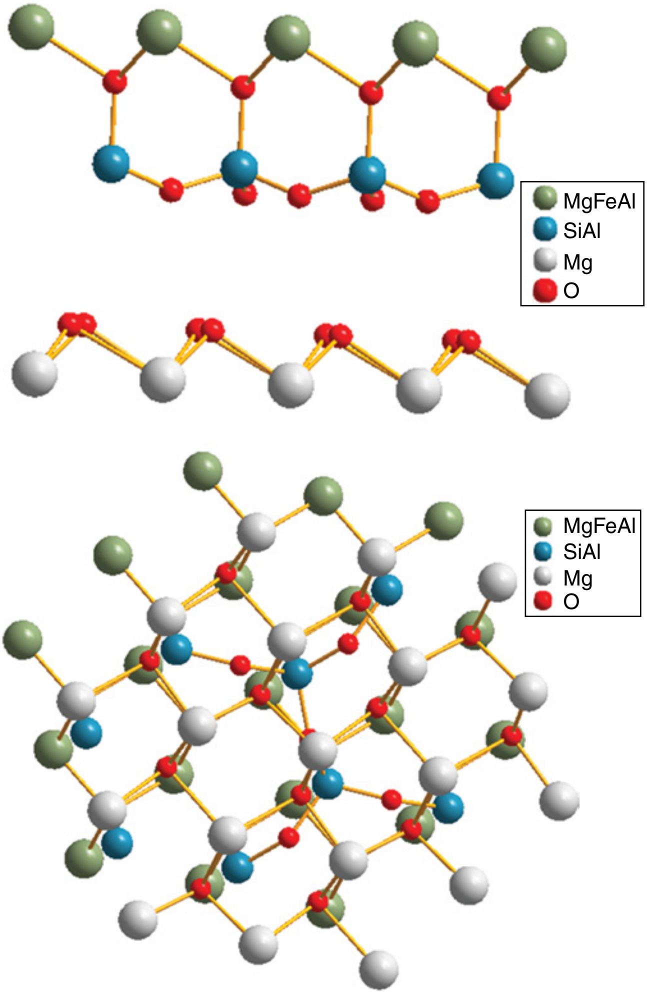

Figure 6.7 *Crystallographic structure of vermiculite*

of veminculite is illustrated in Figure 6.7. Vermiculite has a higher layer charge than smectite clays and a high CEC (The Australian Clay Mineral Society, 2013). The incomplete conversion of vermiculite into organophilic clay allowed simultaneous sorption of anionic radioiodine and cationic radiocaesium and radiostrontium (Hoeffner *et al.*, 2005). Vermiculite is used as additive for sludge and organic wastes (Sinha *et al.*, 2009; Reddy *et al.*, 2010).

Illite has a mica mineral structure composed of tetrahedral–octahedral–tetrahedral layers. Figure 6.8 illustrates the molecular structure of illite. Illite was found to have a retarding effect on caesium release. This effect is caused by the existence of the gap between the illite layers that allows caesium ions to diffuse between the silicate sheets essentially irreversibly retaining these ions.

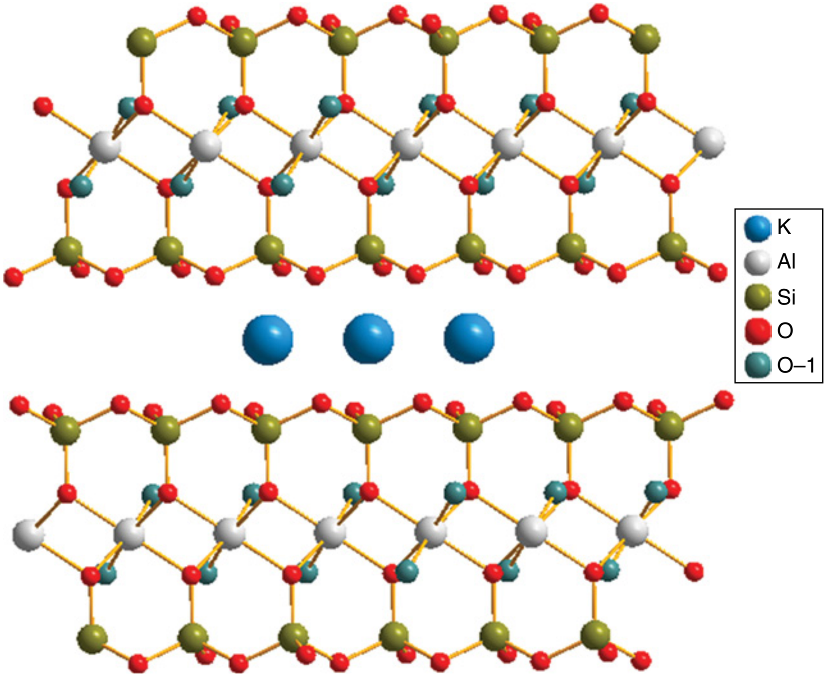

Figure 6.8 *Crystallographic structure of illite*

6.6 Cement-Based Composite Materials

Some novel cements have a history of commercial use in the construction industry, for example rapid-set road and runway repairs and rock anchor bolts, and have already demonstrated persistence in the natural environment. Currently, research into non-nuclear applications of geopolymers is active and is likely to generate more knowledge of their formulation and, in particular, their long-term durability.

Calcium sulphoaluminate (CSA) cements have variable compositions with tetracalcium trialuminate sulphate as the main component, as discussed in section 4.2. CSA was proposed for the immobilization of incineration ashes (Coumes *et al.*, 2013). The hydration of CSA cements was found to be less retarded than for OPC in the presence of zinc chloride and the formation of ettringite and calcium monosulphoaluminate provided good containment for zinc ions due to their flexible structure. Adding 20% gypsum to CSA can accelerate the hydration, reduce the produced cumulative heat and improve the mechanical performance of the matrix. Zinc waste containment in the matrix was found to be as a result of sorption of zinc onto aluminium hydroxides and calcium silicate hydrate.

SIAL is mixture of alkali silicate (sodium, potassium) and metakaolin calcined at 700–750°C. It consists of silicon, aluminium, calcium, sodium, potassium, ferrous and titanium oxides. A polycondensation–geopolymerization reaction is needed to create a three-dimensional network of amorphous structure from the silicon and aluminium tetrahedral coordination. The lattice is characterized by its charge that attracts alkaline or alkaline earth ions to balance it. SIAL has acceptable mechanical and containment performance with a sludge and sludge/resin loading up to 17.5 wt% (Lichvar *et al.*, 2013).

Hydroceramic cement is a cementitious wasteform developed for waste containing high sodium, hydroxide, nitrate and nitrites typical for legacy sludge at the Hanford site, USA. The wasteform is prepared by adding metakaolinite, vermiculite, sodium/calcium sulphide and water at hydrothermal conditions (500–600°C) to convert the inorganic components of sludge into a coarse-grained interconnected multiphase material that has a ceramic-like structure. This wasteform is characterized by low content of an amorphous calcium silicate hydrate phase (Pacific Northwest National Laboratory, 2010).

6.7 Cement-Based Wasteform Optimization

As shown in the previous sections, a large number of cementitious wasteforms have been developed to solidify and stabilize different radioactive waste streams. During the planning phase for cementation, factors that affect the product performance are studied. An extensive array of research has been conducted worldwide to find the optimum water/cement (w/c) ratio, select suitable mix ratios, accelerate or retard cement hydration and study the effect of these parameters on the mechanical and containment performance of the final wasteform. In this section recent advances in the optimization of cementitious wasteforms are presented.

Various experimental techniques have been used to optimize cementitious wasteforms. The Taguchi technique was widely used as a part of the Taguchi quality control methodology adopted in manufacturing for more than three decades to robustly design a product or a process. The Taguchi algorithm converts the quantitative assessment of a specific process into a signal to noise ratio. The ratios are then used to quantify the ability to achieve the target value for the process while minimizing the variation from the target for specific experimental conditions (Pan *et al.*, 2007). The application of this technique includes three parameter designation steps as follows (Pan and Chang, 2004):

1. Identification of mutually interactive dominant parameters.
2. Revision of dominant parameters to ensure precise quantification, thus fine-tuning of quantities is more vital than determining dominant parameters.
3. Verifying process evaluation, which produces a more accurate quantity of interested parameters.

The optimization of spent ion exchanger cementation was studied using the above-mentioned three-step method. The target performances were the compressive strengths and bending tolerances. The results indicated that the best mixture for furnace slag–fly ash–cement–resin–water was with the ratios 30:26:9:13:22 wt% (Pan and Chang, 2004).

The optimization of cementitious matrix for the immobilization of metal oxides was conducted with varying cement types, waste loadings, w/c ratios and oxide densities (Coumes and Simone, 2006). The results indicated that by increasing the waste loading in the paste from 1 to 10 wt% increased swelling under water, irrespective of the other factors. Cement type CEM1 was found to produce a more stable matrix than other types; on the other hand, the rest of the factors have a negligible effect on the performance of the matrix. Swelling reached its maximum when low-density oxide was incorporated at a level of 10 wt% with w/c=0.45.

Optimization of parameters that affect radiation attenuation in normal- and heavy-weight concrete was conducted accounting for w/c ratio, curing condition, cement quantity and air-entraining agent. Eight energy values were selected within the energy range of 30.85–383.85 keV to be used in calculating radiation source shielding. The study revealed that the w/c ratio is the most important parameter and that concretes having the lowest w/c ratio absorb most radiation (Sahin *et al.*, 2011).

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7

Waste Cementation Technology

Different waste cementation technologies have been suggested and developed to immobilize nuclear wastes. The selection of any of them relies on many considerations such as waste characteristics, cement handling techniques, mixing methods and equipment complexity and maintainability. The type and quantity of the waste emitters plays an important role in the optimization of shielding systems. For examples, gamma emitters require a heavier shielding system. Accordingly, the design of the shield can vary from a simple shield installed around the cementation system to keeping the whole cementation system in a shielded area.

Waste cementation technologies are primarily differentiated by the mixing method; two basic classes are widely used [International Atomic Energy Agency (IAEA) 1992, IAEA, 1993a, b, 1994]:

1. In-drum mixer for the cementation of liquid wastes, sludges and ion-exchange resins.
2. Grout batch mixer for the immobilization of solid wastes and for grout capping.

The following sections will present information related to available waste immobilization technologies, their features and applicability to different waste streams.

7.1 Methods of Liquid Waste Cementation

In-drum mixing is the most widely used method to immobilize sludges arising from liquid effluent treatment. The IAEA suggested the utilization of in-drum mixing technology. The cementation unit is composed of the following (IAEA, 1994):

- Electrically driven mixer that could be raised and lowered.
- Polypropylene sludge hopper.

Cementitious Materials for Nuclear Waste Immobilization, First Edition. Rehab O. Abdel Rahman,
Ravil Z. Rakhimov, Nailia R. Rakhimova and Michael I. Ojovan.

- Side clamps; these should be provided to prevent drum movement during mixing.
- Splash guard; this raises and lowers with the mixer, and covers the drum when being in lowered position. This guard features cut outs for the sludge feed pipe, and for cement feed via a shaft/funnel.

Operation of this unit starts by transferring sludges from the sludge tank to the sludge hopper using a diaphragm pump via a PVC line (Figure 7.1). The hopper is recommended to have a nominal working capacity of approximately 150 L, and is approximately 0.6 m in diameter and 0.8 m tall for managing small amounts of radioactive wastes. Pipe-works and valves exist to allow the hopper either to be discharged to a drum for cementation or to be returned to the sludge tank. The sludge tank is calibrated, with an overflow back to the sludge tank at a height equivalent to one single batch of sludge held in the hopper. When this height is reached, or the hopper begins to overflow, the pump is stopped. Having ensured that the hopper delivery pipe is in the drum, the hopper discharge ball valve is opened and sludge is transferred into the drum (IAEA, 1993b).The stirrer of the mixer is then started, and a premeasured batch of cement is then slowly added to the sludge, stirring the batch continuously. When mixing is finished, the cement and sludge feed lines are removed, and the splashguard lifted. The stirrer is then raised and left for a defined time to drip. After this time, the mixer equipment is moved away from the cemented sludge drum and positioned around a previously prepared drum of water. The mixer head is lowered and the mixer operated for 2 min to wash the stirrer. After mixing, the cemented sludge drum is temporarily lidded and left to stand without moving for 24 h to allow the mix to set. The next day the drum contents are tested

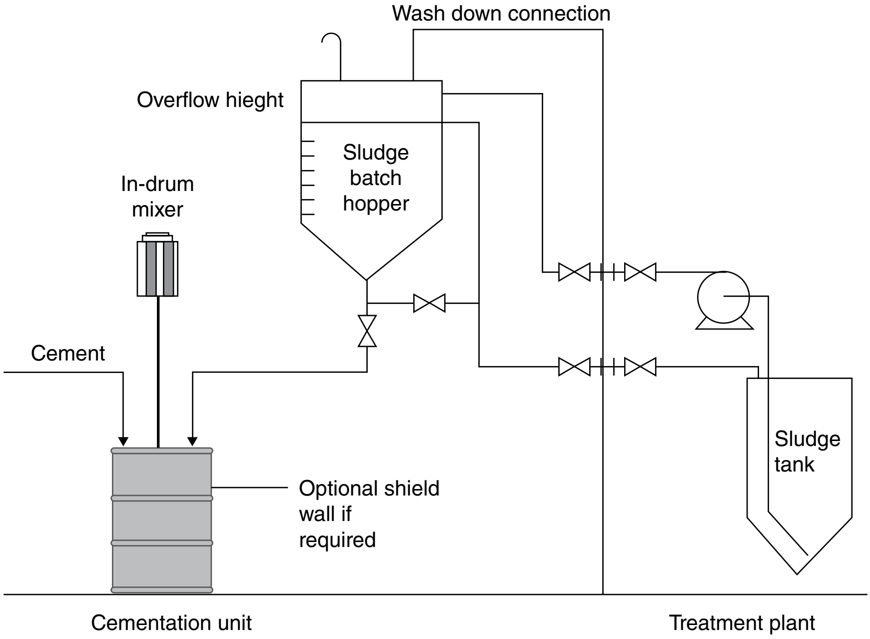

Figure 7.1 Schematic flow diagram for in-drum mixing for sludge. Reproduced with permission from IAEA, 1994. © 1994, IAEA

for set by using a penetrometer, and any bleed water is removed by pumping to a small container. Bleed water is then transferred to the small tank of the liquid effluent treatment plant. A small batch of grout is prepared and pumped or poured onto each drum until the surface is within 2.5 cm of the drum lip. The grout cap is allowed to set for 24 h, tested for set and then the drum lid is finally fitted. The sludge transfer and overflow lines and the hopper should be washed out with small batches of water at the end of the process. Wash water then is directed to the sludge lines to drain into the sludge tank from where it can be pumped back to the precipitation tank for treatment. Wash water directed to the sludge hopper should be collected in a carboy and taken to the laboratory for transfer to the small arising tank as for other small quantities of aqueous liquids (IAEA, 1994).

7.1.1 Regular Mixer Technology

The Stock Equipment Company has developed an in-drum mixer for cementation of low-level wastes as illustrated in Figure 7.2. In this technique, five steps are performed starting by adding dry cement in a 55 gal. drum outside of the shielded area then the treated wastes are added with the chemical in the shielded waste processing area. The drum is moved behind the shielding wall where the waste and any additional chemicals are added. The drum is then remotely capped and tumbled end-over-end in order to thoroughly mix the contents (Fuhrmann *et al.*, 1981). The wasteforms produced at Brookhaven National Laboratory incorporate low-level radioactive waste in a mixture of Portland cement and vermiculite. Wastes solidified in this manner include liquid evaporator slurries, compacted trash and 55 gal. drums containing ion-exchange resins. Cement and vermiculite (and large solid wastes, if any) are placed into the steel reinforced, precast concrete casks (15 cm thick walls, 4.5 m capacity). Liquid waste is pumped into the cask through pipes embedded in the dry cement, with the vermiculite serving as a sorbent and water distribution agent. When the surface of the vermiculite and cement mixture appears moist, pumping is stopped. A steel reinforcing grid is placed on top of the cask and premixed uncontaminated concrete is poured as a seal. In a typical cask, 0.9 m of concrete are used to solidify 1.25 m liquid waste (Fuhrmann *et al.*, 1981).

In Serbia, sludge immobilization is performed using 200 L metal barrels. The barrels are shielded using a 6–7 cm concrete layer followed by a 1 cm plastic layer that is coated with epoxy. The useful volume of the barrel is about 75 L (Pesic and Plecas, 2011). The planned immobilization process is as follows:

- The radioactive waste will be transferred from a nuclear reactor spent fuel storage pool to a sedimentation tank, then 60–65 L of sludge will be poured into the barrel and covered.
- The sludge will be allowed to further settle and the separated water will be pumped into a plastic can and returned to the reactor spent fuel storage pool.
- The settled sludge (about 40 L) in the barrel will be placed on the platform of the mixer and PC-45 MPa cement will be added to achieve a 1:1.8 sludge to cement ratio.
- Cement will be mixed with sludge and left for solidification.

Figure 7.3 shows the technological scheme of combined liquid and solid waste immobilization in drums at FGUP RADON in Russia (Ojovan and Lee, 2014). This method uses cement grout prepared by mixing aqueous radioactive waste with cement powder and optional additives.

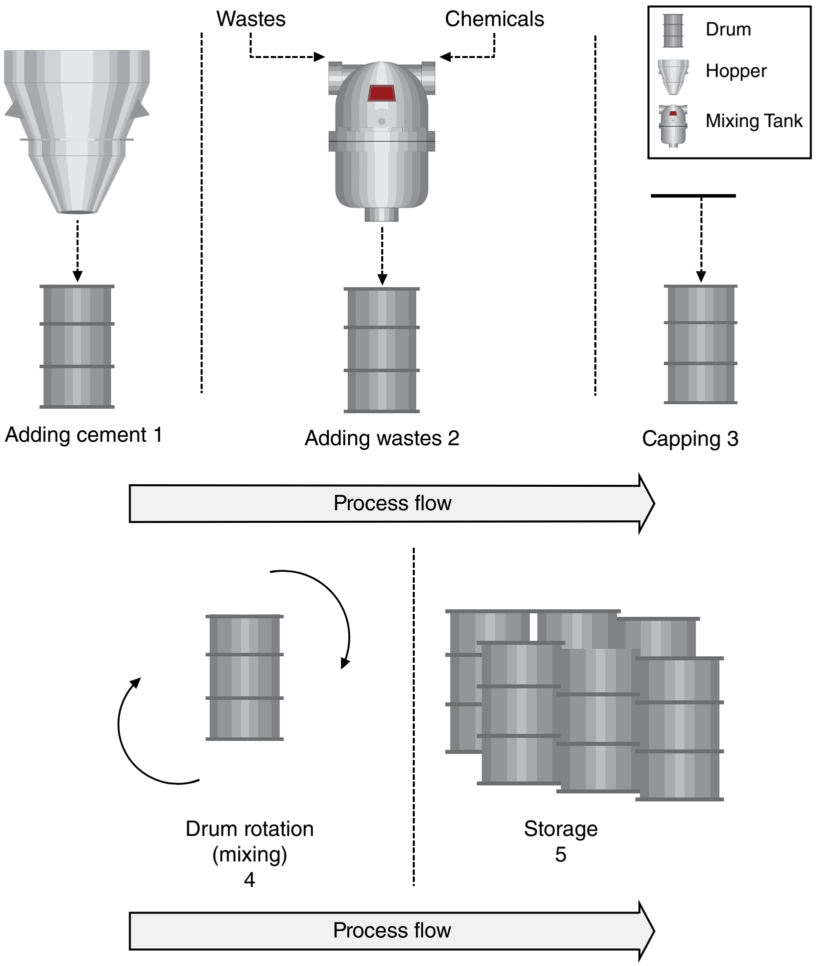

Figure 7.2 Five steps in drum mixing processing for incorporating low-level wastes in cement

A high performance in-drum mixer has been installed at the Research Centre Karlsruhe, Germany as a permanent cementation unit. The unit is arranged inside a hot/warm cell. Depending on the radiation level, the machinery is operated by remote manipulators or hands-on through gloves fitted on the cell. To ensure high shear dispersion and compensation of torque force that might be transmitted to the drum, the mixer is provided with two counter-rotating cylindrical helices. The mixing unit is characterized by its rotation to ensure that the helical blades sweep the entire circumference of the drum. After usage, the mixing elements are raised and decontaminated by:

- letting the elements drain into the drum;
- using a hand-held vibrator after curing of the residue;
- rotating them in a decontamination solution.

The utilization of this system in mobile application, known as DEWA, has been successfully applied at three nuclear power plants (NPPs) in Germany; the steps of this

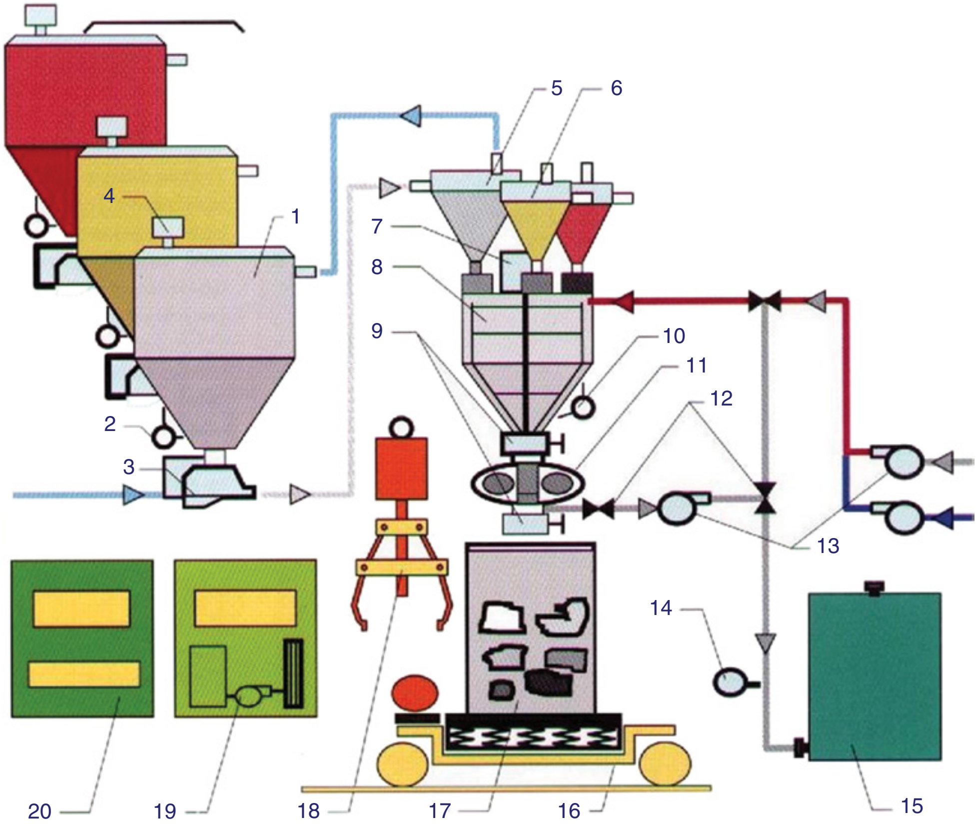

Figure 7.3 Schematic of a modular cementation plant: 1, cement and additives bunkers; 2, vibrator; 3, jet pump; 4, air valve; 5, cement service bunker with batcher; 6, additives service bunker with batcher; 7, mixer drive; 8, tank with mixer; 9, hose bolts; 10, vibrator; 11, vortex type mixer; 12, valves; 13, pump-batchers; 14, manometers; 15, cartridge filter for impregnation; 16, vibrating platform; 17, drum with solid waste; 18, crane; 19, vortex mixer service desk; 20, control desk. Reproduced with permission from Ojovan and Lee, 2014. © 2014, Elsevier

process are illustrated in Figure 7.4. The unit is shipped using a flatbed trailer, and unloads by telescopic legs which are swung into position. It is composed of a cube-shaped frame in which a steel-shielded hot cell is arranged. Its operating system is supplied with a control panel and a roller conveyor to transfer the drum beneath the docking hole of the mixer, where the docking device lifts the drum and seals the rim to the mixer. An ultrasonic level sensor and Coriolis flow meter are installed in the unit to measure and control the mass flow (NUKEM, 2007).

7.1.2 Disposable Stirrer Technology

The utilization of disposable stirrers instead of fixed stirrers is widely applied throughout the world. This technology minimizes secondary wastes produced during the decontamination of the stirrer. Historically, different fixed disposable stirrer units were installed during the

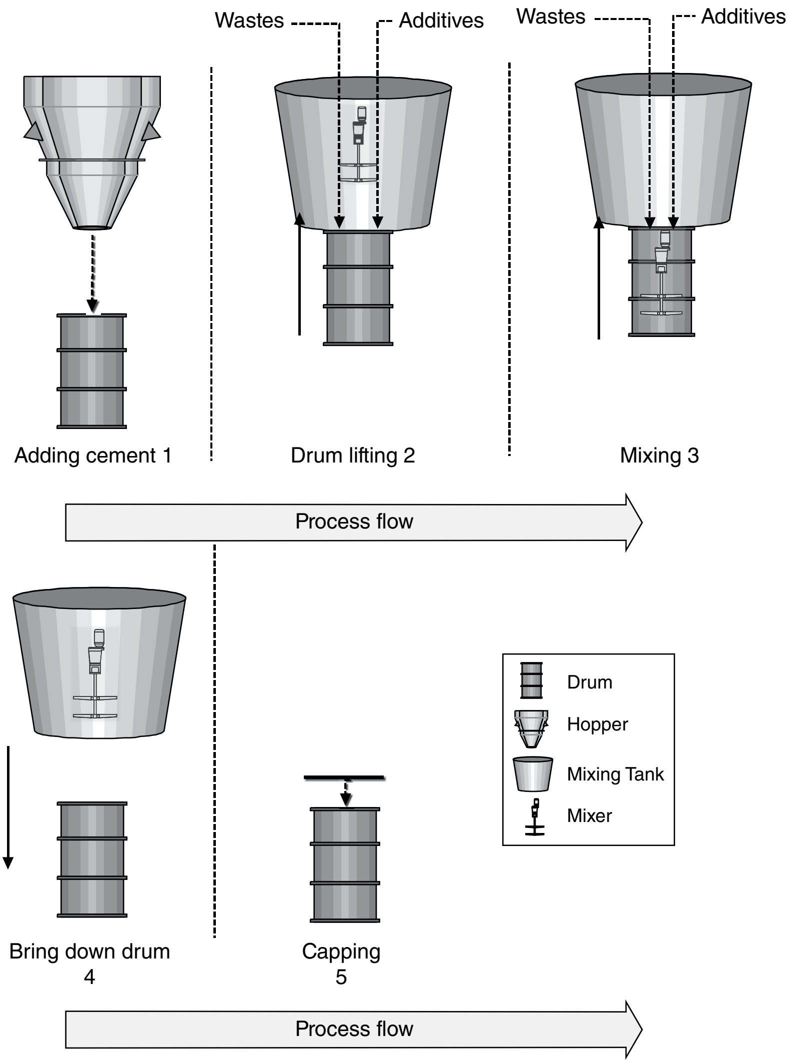

Figure 7.4 *Process flow inside a DEWA mobile system*

operation phase at UK NPPs (e.g. Trawsfynydd and Hinkley Point A) and research and processing sites (i.e. Sellafield and Dounreay). It is worth mentioning that Trawsfynydd and Hinkley Point A NPPs are now in the decommissioning phase and different grout systems are being utilized to immobilize the nuclear wastes produced. In the USA, Delaware Custom Material, Inc. has developed an in-drum mixing process in which disposable rotor blades are turned within a 55 gal. drum by a pneumatic motor as the cement and waste are added, as illustrated in Figure 7.5 (Fuhrmann *et al.*, 1981).

In Sweden, this technique has been applied since 1972 in a fixed immobilization unit at Oskarshamn 1 NPP. Currently, this technique is installed in several Swedish NPPs (e.g. Ringhals 1, Oskarshamn 3, Forsmark 3 and Mühleberg). It was found from operating

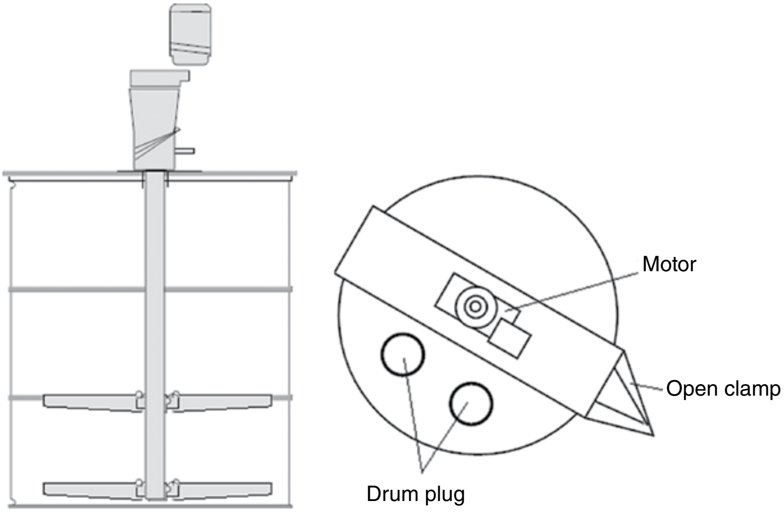

Figure 7.5 *Disposable dual bladed in-drum mixer*

this technology that the process is a clean process as few components are exposed to radioactive waste (Gesser *et al.*, 2000).

The disposable dual bladed in-drum mixer is widely used; generally the waste and additives are added followed by the cement. Figure 7.6 shows the general process flow for waste cementation using a disposable dual bladed in-drum mixer.

The immobilization of liquid wastes produced during the processing of MTR and CANDU fuel at EUREX and ITREC in Italy is performed using similar cementation plants, CEMEX and ICPF, respectively (Paratore, 2011). The acidic wastes are neutralized with NaOH and metered in 440 L drums; the cement is added while the solution is stirred by a disposable stirrer.

Mobile commercial units that utilize disposable stirrers have been developed and are currently widely used, for example MOSS (mobile sludge solidification), MOWA (mobile waste) and TILWSP (Transportable Intermediate Level Waste Solidification Plant). The MOSS unit was developed in Sweden and has been used in different countries to immobilize various wastes. The unit is hosted in a shielded room that is suitable to immobilize wastes that exhibit moderate levels of gamma radiation and low levels of alpha activity. The shipping container includes the following (Crawford *et al.*, 2011):

- drum trolley and its hydraulic power unit;
- local ventilation system;
- daily cement tank;
- additive dosing tanks and pumps;
- drip pan and trolley rail system;
- control panels.

MOWA is a small mobile unit designed to deal with different sized drums (100–400 L). It has two dosing and mixing positions, a sealed cell for the wastes, two hydraulic units for the stirrer drives and a control panel. Heavy lead shield is provided for the equipment that

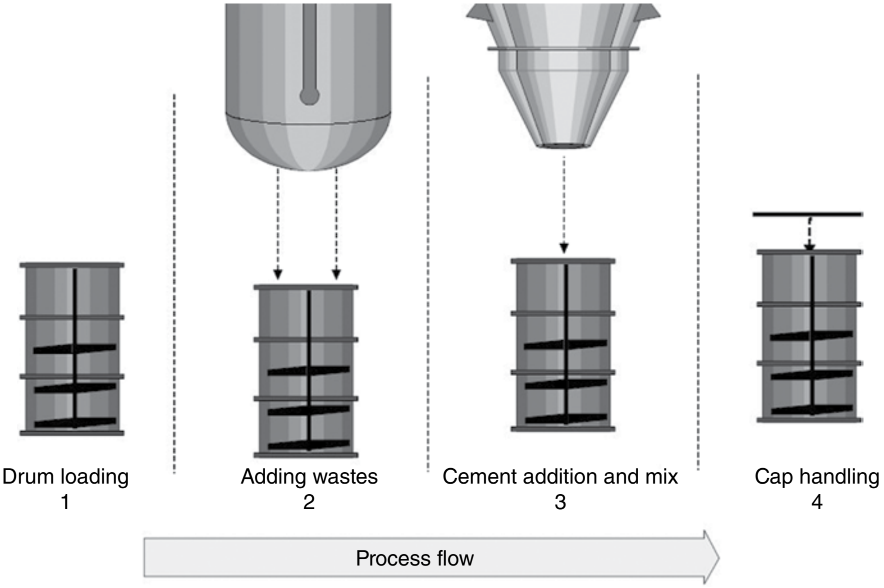

Figure 7.6 *Process flow for waste cementation using a disposable dual bladed in-drum mixer*

handles radioactive wastes, where the mixing position is shielded with a steel shield to reduce worker exposure to less than 10 mrem/h at the surface during the immobilization of wastes with activity up to $3.7\times10^{13}\,\mathrm{Bq/m^3}$ (NUKEM, 2007). The drums connect first for waste feeding with an air outlet and disposable stirrer provided. Thus, the entire mixing process takes place within an enclosed system to avoid the spread of contamination. The waste could be introduced to the unit by vacuum or fed by an external pump, then transferred into the cement pre-filled drums by means of another pump. Mixing takes place in the drums during feeding and the displaced air is released through high-efficiency particulate air (HEPA) filters. After the completion of the mixing, the drums are fitted with a second cover which is located below the upper rim.

The TILWSP unit was developed by BNFL, UK for waste solidification and packaging operations at Magnox power plants. It consists of a number of separate modules built into ISO freight containers that can be transported for use at different sites (Figure 7.7). The plant is shielded and provided with a control panel to operate the unit remotely. It is designed to immobilize spent ion-exchange resins, sludges, desiccants and other wet wastes resulting from reactor operations. Waste is loaded into a $3\,\mathrm{m^3}$ drum and mixed with cement powder to produce a homogeneous monolithic paste which solidifies. It has been used at Trawsfynydd NPP since 2003 to immobilize sludge wastes from the cooling pond and effluent treatment system (Nirex, 2005). It is worth noting that although this unit was developed as a mobile unit, it is currently used as fixed unit at Trawsfynydd.

The MILWPP (Modular Intermediate Level Waste Packaging Plant) is a mobile unit that was designed to immobilize intermediate level sludges from the spent nuclear fuel storage pond building (B30) at the Sellafield nuclear processing site in the UK. B30 is a legacy early generation fuel decanning facility for the UK Magnox reactor's uranium metal fuels. As

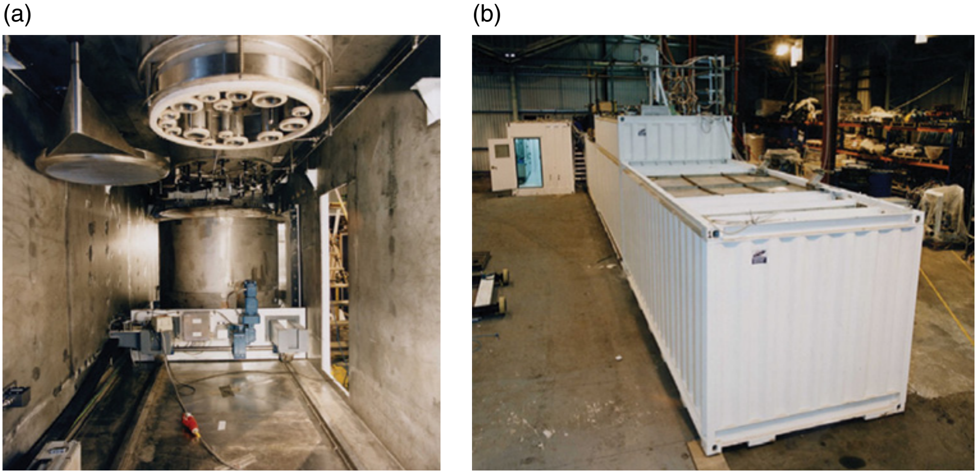

Figure 7.7 The TILWSP unit: (a) internal configuration; (b) external view. Reproduced with permission from Nirex, 2005. © 2005, NDA

a result of the long underwater storage of the fuel at the facility, the sludges in B30 are rich in uranium metal and fission products from decanning processes and uranium oxides from corrosion of fuel. Handling and grouting of this waste is therefore a significant challenge (Nirex, 2005). The MILWPP unit is located inside a cell made of transportable modules; the walls and ceiling are designed to enhance radiation shielding from alpha- and gamma-emitting radionuclides and provide contamination confinement. The unit is provided with a fully enclosed, ventilated cell arrangement protecting operators from the waste but allowing most equipment to remain external to the shielding and so be readily accessible for maintenance. The drums are elevated to various heads using two independent trolleys which work in concert with a pair of channels running the length of the MILWPP unit allowing the trolleys to lower, park their drums and traverse to service other drums. The two trolleys ensure that the two drums which at any time are undergoing active operations are always raised up to the ventilation heads, except during transfer to the next station. This minimizes the potential for contamination of the MILWPP interior.

7.1.3 Slant Mixer Technology

Slant batch mixer technology has been installed at several waste treatment centres. Typical commercial units using this technology are provided with a variety of auxiliary systems (resin dewatering unit, ash transfer and metering). Sludges are pumped into the waste receiving tank from the waste treatment facility, then flow by gravity to the metering tank. Cement powder is loaded into a cement silo, from where it is transferred into the cement-metering tank. Additives required are weighed on a scale and put into the additive tank (NUKEM, 2007). The cementation line at Bohunice Conditioning Centre, Slovakia uses a slanted mixer. At this Centre, the concentrated waste enters the dosing tank of the cementation line directly from the concentration device or via the inlet of ion-exchange resin accumulators. The dosed waste and cement are then directed to the slanted mixer (500 L). After a thorough mixing the cement mixture is directed into a fibre-reinforced concrete container (3.1 m^3). Six batches from the mixer are required to fill up the container. Containers with firm cement are closed, checked and shipped to the National Radwaste Repository at Mochovce, Slovakia. When the container is filled up with drums of bituminized product or compacted pieces of solid radioactive waste then three batches from the mixer are needed to fill up the remaining free space in the container (National Report of the Slovak Republic, 2003).

7.1.4 High Energy and High Shear Mixer Technology

Keller Colcrete successfully pioneered the development of the high-shear colloidal mixer in 1937 and for over 70 years it has been internationally recognized as the most efficient method of mixing cement-based grouts. These mixers are used by the British Nuclear Industry (BNI) for the preparation of special grouts used for the encapsulation of medium- and low-level radioactive wastes (Reschke, 2000).

To optimize the control and reliability of the slurry cementation process at the Liquid Effluent Treatment Station at Marcoule by 2015, the French Energy Commission (the CEA) has undertaken an extensive development programme on a semi-industrial scale cementation pilot platform. The platform comprises three levels representing a surface area of approximately 200 m^2. The upper level is for batching and introducing various components in the high energy mixer installed on the intermediate level. The lower level is reserved for the docking and maintenance of the canisters. A characterization laboratory also forms part of the platform (Cardinal *et al.*, 2013).

7.1.5 In-line Mixing Technology

In-line mixing processes combine the waste, additives, water and cement before they are placed into the container or drum. Ribbon mixers and pug mills, among others, may be used to mix the waste and cement. Figure 7.8 illustrates the United Nuclear Industries, Inc. in-line system as an example. Here preconditioned waste, adjusted for moisture content and pH, and the cement are blended at a mixing pump. Additives can be introduced at the fill port (Fuhrmann *et al.*, 1981).

7.2 Methods for Cementation of Fragmented (Dispersed) Solid Waste

A simple grout batch mixer is used to prepare grouts for in-drum grouting and grout capping. The IAEA indicated that in-drum grouting equipment could be used to immobilize non-compactable solid wastes and spent sealed sources. Non-compactable waste drums are moved from the sorting cabinet into the cementation area using a manual fork lift truck, and placed adjacent to the grout batch mixer. A batch of grout is prepared in the mixer, grout is then transferred using a pump or by pouring into the drum. The grout should be introduced at three or four positions around the drum to ensure all voids are filled. The mixer should be electrically driven, mobile and capable of producing batches of up to 200 L. There are different commercial types available; Figure 7.9 illustrates a helix cement mixer for centralized waste processing and storage facility. Batches of grout can be poured from such a mixer either directly into a drum or via another container (IAEA, 1994). It is worth mentioning that for immobilization of

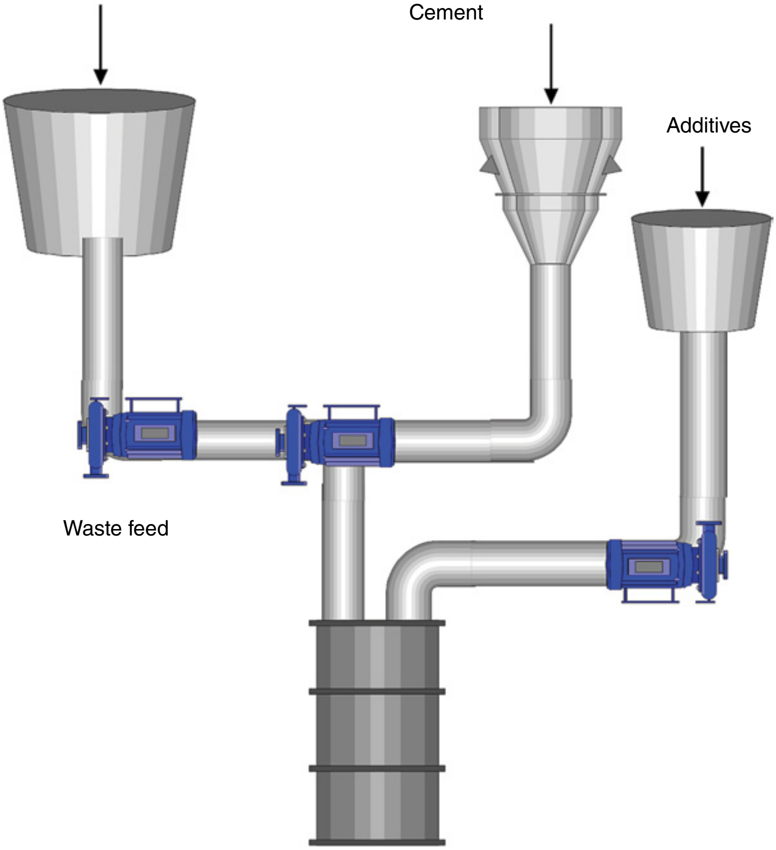

Figure 7.8 *In-line mixing with additive*

ion-exchange resins the waste loading is small. The loadings can be increased by a pretreatment, such as grinding spent ion-exchange materials before cementation, which improves the quality of the final cemented products. A disadvantage of cementation for organic ion exchangers is the swelling of resin beads after contact with water, which can lead to subsequent micro cracks in the cement. The IAEA reported that owing to their size being less than 0.1 mm, an overall cracking of the cement structure does not occur with powder resins. The cementation of spent bead resins without a pretreatment such as grinding should therefore be avoided (IAEA, 1993b). The immobilisztion of inorganic ion-exchange resins, such as oxides of titanium and manganese, the phosphates of titanium and zirconium, polyantimonic acid and copper hexacyanoferrate, were also studied. It was found that, with each of these absorbers, 33 wt% waste loading can be reached, with a good quality of solidified product (IAEA, 1993b).

In the MOWA unit, ion-exchange resins are prepared for cementation by adjusting the stipulated water to resin ratio in the resin metering pot. This pot is equipped with a slot sieve base to drain the excess water. The resin is then pumped with exactly the excess water required for cementation into the drum in the same manner as sludge. After being sealed remotely, the waste drum is replaced by a new one (NUKEM, 2007).

Figure 7.9 *Typical cement mixer for centralized waste processing and storage facility. Reproduced with permission from M. Ojovan*

Slant batch mixer technology can be used to immobilize ion-exchange resins, ashes and concentrate. The resins with water are transferred hydraulically and received under pressure in the resin receiver tank. There, excess carrier water is separated by means of built-in slot sieve filters. This water is returned to the transport vessel. The ashes enter the cementation facility and are held in suitable containers. These containers are emptied into the metering pot for ashes within the transfer box. The solids to be encapsulated (e.g. compacted solid waste) are put in the long-term storage container before entering the cementation facility. The remaining free space is usually more than 50% of the container volume (NUKEM, 2007).

Although stirrer mixers provide a good quality of mixing, high shear colloidal mixers have been also used. Colloidal mixers use the combined effect of the highly efficient mixing action and the ability to mix materials at low water/solids ratios, thus allowing for reductions in the cement used to obtain a required strength of wasteform (Paratore, 2011). This technology is widely applied for grouting solid radioactive wastes (NUKEM, 2007).

The CILWPP (Canyon Intermediate Level Waste Processing Plant) is an encapsulation module that was designed to serve the retrieval and encapsulation activities of the wet intermediate-level waste at Hunterston A NPP, UK (Crawford *et al.*, 2011).The unit allows automated operations and accepts 3 m^3 drums to meet regulatory requirements in the UK. The CILWPP is shielded with blocks placed around the encapsulation equipment but has no ceiling overhead which makes it only suitable for applications where the waste stream emits low to moderate levels of gamma radiation and where airborne activity is not a significance issue. Within the plant, the wastes can be received and encapsulated in a cementitious grout and the grout set is verified. The unit adds a cold capping grout, swabs the drum around the lid flange for contamination, lids the drum and handles the product drums. Similar to the MILWPP unit, the CILWPP contains six stations to load, fill, perform quality assurance test, cap and lid the drums and also a spare station. The plant utilizes lime, ordinary Portland cement (OPC) and pulverized fly ash (PFA), and OPC and blast furnace slag (BFS) powders in grouting. The immobilization process commences by adding waste to the drum in the form of sludge slurry, resin slurry or neutralized acid. Following waste addition, hydrated lime powder is added to the waste. It is then followed by appropriate quantities of two dry mixtures of OPC and PFA or OPC and BFS powders to ensure effective solidification. The drum weight is monitored and feedback is provided on the amount of materials added. The drum paddle is driven by a compact hydraulic motor to provide the required torque to mix the drum contents for the duration and speeds predetermined by the operator. A local ventilation system at the fill-head is in continuous operation regardless of fill-head position, exhausting through a common vent header to dedicated HEPA filters before being discharged into the main facility ventilation system. The fill-head also features various air and water rinse capabilities, and a camera with auxiliary lighting to view the solidification process in the drum as it occurs. Redundant ultrasonic level detectors are provided to minimize any possibility of overflow. A diagram of the CILWPP fill-head assembly is illustrated in Figure 7.10. The capping station contains an ultrasonic level detector for determining the grout level in the drum. Dedicated and spare feed lines are provided for grout addition; they are composed of a flexible Tygon inner hose surround by an outer flexible, poly-lined hose to facilitate inner hose removal/replacement. The expansion characteristics of the inner hose are desirable when cleaning the line with pressurized air before and after grout pumping with the line expansion also tending to keep the lines clear of hardened grout. The drum lid is introduced and fastened on to the drum at the drum load-out/lidding station; the drum package is then verified to be free of external contamination and the drum is removed from the system. A lid with mounting bolts is fed manually into a lid grapple suspended from a jib crane which swings the lid over to the drum. The lid grapple is keyed so that the lid cannot be misaligned with the drum, while sleeves on the grapple retain the bolts. A pair of manipulators viewed by CCTV cameras aid the lid placement, and the lid bolts are tightened using a computer controlled nut runner designed to both measure and control torque (Crawford *et al.*, 2011).

AGCMS (Glovebox Cementation Mixing System) was designed to address the need to deal with high alpha inventory of low- and high-level active waste effluents from the MOX fuel fabrication facility and the pit disassembly and conversion facility at the Savannah River Site, USA. The system uses a lightly shielded but highly confined glovebox to produce wasteforms within 55 gal. drums without spreading alpha activity. AGCMS can be permanently installed in facilities where an ongoing process is in place or conversely is compact enough to permit mobile use. This system relies on disposable stirrer technology; the key design parameters were identified to include cement preparation methodology, waste addition rate, paddle torque, paddle speed and mixing

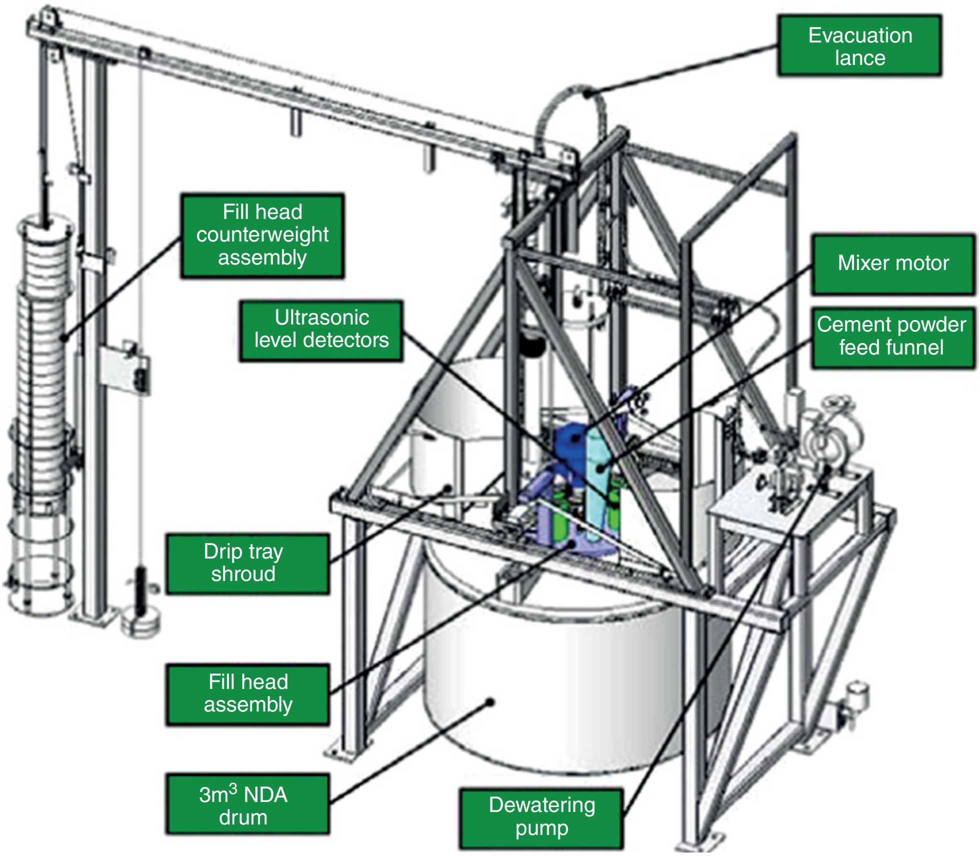

Figure 7.10 Main stations at UK mobile unit CILWPP. Reproduced with permission. © 2014, G. Crawford

durations. Robust drum clamping and sealing techniques during mixing and drum confinement effectiveness were demonstrated. A replaceable off-gas roughing filter is used to protect the operator downstream of HEPA filters from trace cement dust carried into the off-gas. The unit utilizes integrated bagless transfer coupling, waste fill line and cementation drive between the glovebox drum and the waste drum. This bagless transfer confines the active waste solely within the drum and the primary confinement ensuring that the exterior of the drum and the interior of the secondary confinement surrounding it are segregated from the waste throughout the drum positioning, filling and mixing processes. The diagram of key mechanisms in the GCMS is illustrated in Figure 7.11. The unit has three confinement levels as follows (Crawford, 2010):

1. Transition confinement at the inlet and outlet airlocks.
2. Primary confinement where waste is introduced into the drum. This section of the glovebox can be contaminated and operates at a gauge pressure of approximately –1.0 in. water column.
3. Secondary confinement sits below the primary confinement where a lift moves the drum up to the underside of the primary confinement. This section is not exposed to contamination under normal conditions and operates at a gauge pressure of approximately –0.7 in. water column.

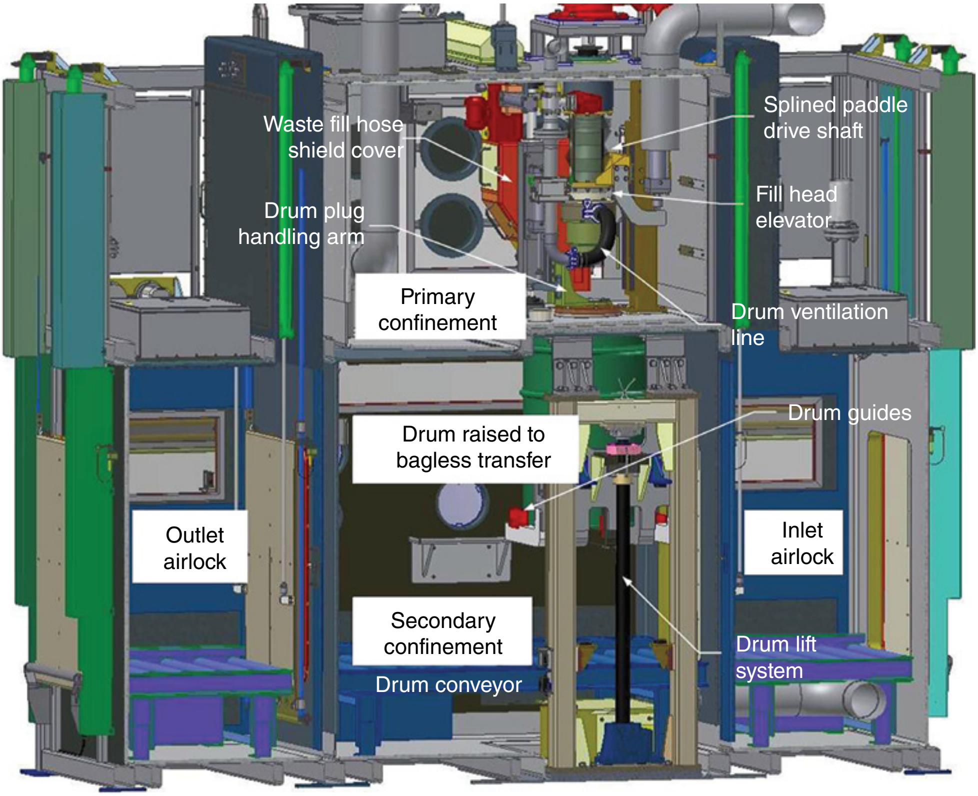

Figure 7.11 *Confinement units of the GCMS. Reproduced with permission. © 2014, G. Crawford*

The effectiveness of immobilizing lump and fine dispersed solid radioactive waste within a special cementitious composite matrix is used at FGUP RADON, Russia (Varlakov, 2013). Lump solid radioactive waste was proposed to be immobilized by top grouting of containers with waste with fine dispersed and close packed solid radioactive wastes immobilized using the bottom impregnation method. Top grouting method is conducted by placement of lump waste in the container followed by cement grout pouring from the top. The grout should be characterized by high flowability to penetrate into air holes between waste pieces. For bottom impregnation, a feeding pipe is introduced into a container with fine dispersed or close-packed waste and highly penetrating cement grout is pumped through it to the bottom of the container. Cement grout gradually replaces the air, penetrating into gaps and pore spaces; it gradually and evenly fills in the free volume forming a durable monolith after hardening.

7.3 Methods for Cementation of Bulk Solid Waste

Bulk solids refer here to any part of a nuclear facility that may be removed without being cut. Bulk wastes can be conditioned in a non-standard package for disposal or storage and therefore requires specific consideration by local regulators due to its weight, volume or the extent of its radiological contamination. This implies that related standard processes by the operator to manage transport, storage or disposal cannot be directly applied and need to be modified. Bulk solid waste may include steam generators, pressurizers and reactor vessels and heads (NEA, 2012).

Historically, four reactor compartments with eight reactors (three containing damaged fuel) were dumped in the Abrosimov Gulf. The compartments had been cut out of submarines and closed at both ends; they still contain reactors with spent fuel. The compartments had been filled with protective material of steel, cement and polyester to prevent radioactivity seeping out into the marine environment. According to Russian reactor constructors, this protection may last for up to 500 years (Kopte, 1997).

In Belgium, large activated components such as thermal shields and pressure vessels are subjected to remote-controlled underwater cutting. To comply with the regulatory requirements, these components are segmented in pieces having a maximum length of approximately 500 mm and a maximum weight of 560 kg. After packaging, the activated pieces are conditioned into a cement matrix and are currently held in storage (NEA, 2012). CILVA is one of the processing and conditioning plants in Belgium. It is composed of five units (Kingdom of Belgium, 2006):

1. The reception and pre-storage unit for unprocessed radioactive waste (weighting, control of radiation levels and external contamination).
2. Pre-processing unit (waste sorting, cutting and pre-compaction).
3. Super-compaction unit with a 2000 t press to compact the 200 L carbon-steel drums containing the unconditioned radioactive waste.
4. Incineration unit with a capacity of 7.5 t solid waste per week.
5. Conditioning unit to immobilize the super-compacted discs inside the 400 L drums with cement.

7.4 Quality Control of Technological Processes and Materials Obtained

As for any other industrial activity, radioactive waste management needs planned and systematic actions to provide adequate confidence that the entire system, processes and products involved will satisfy given requirements for quality (Abdel Rahman *et al.*, 2007). These requirements have to take place in every activity carried out within the radioactive waste management system to achieve the overall protection goals set by regulatory authorities (Abdel Rahman, 2009). Within a general quality assurance programme for any radioactive waste activity, a quality control system is needed to ensure compliance with both shielding and safety regulatory requirements. In this system each process, within the management activity, that could affect the final quality of the products should be identified and adequately controlled, performed and documented.

Waste immobilization is part of the radioactive waste management system; both direct and/or indirect controls could be used depending on the level of complexity of the process and the sensitivity of the final product to the considered processes. To plan for a quality control system, a proper identification and control on important parameters should be performed and the system could be divided into subsystems. The cementation process could be qualified by controlling the input materials, such as cement, additive, and waste, dosing, mixing and curing processes and the immobilization product (wasteform).

Compliance with the conditions of acceptance could be carried out by indirect and direct inspection of the input material. In indirect inspection, a nominated person carries out the inspection against conditions for input material acceptance using authorized procedures. Guidelines and instructions should be established to control methods of data transmission from the waste treatment facility to the immobilization unit for review and approval prior to shipment; these data include the specific waste properties (i.e. radioactivity, chemical and physical properties). Nonconformance issues raised as a result of this level of control should be evaluated by the assessment committee. Procedures should be developed according to general guidelines defined to describe the conditions of acceptance. Within the direct inspection, waste characterization and/or operation teams should be responsible for implementing waste characterization qualifications to ensure the compliance of the received waste with the conditions for acceptance.

Dosing cement, additive and wastes and mixing parameters can be optimized so that the content of waste can be maximized. Dosing techniques are installed in the immobilization unit to help in assisting this process. In the MOSS unit, the control system can store 10 different recipes. Upon selection of the desired recipe, the amounts of waste, cement and additives are dosed automatically. Thus, the composition in each drum and the predetermined product quality are assured (Gesser *et al.*, 2000).

To control the product at the CILWPP, a quality assurance station utilizes a CCTV camera and a penetrometer to verify the proper solidification of the waste after a minimum curing period of 16 h (Crawford *et al.*, 2011). The penetrometer is slowly pushed by a pneumatic cylinder against the top surface of the grout. The force exerted on the grout is indicated on the penetrometer gauge, which can be read by the operator from another CCTV camera to verify whether the reading is above a prescribed acceptable value for the waste product. The surface of the cured drum is inspected visually using the local CCTV camera and any significant amount of bleed water is removed and pumped to the following drum at the fill station.

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8

Cementitious Wasteform Durability

8.1 Wasteform Durability Requirements

Waste Acceptance Criteria (WAC) set the limits for acceptance of a waste package into a storage or disposal facility. These criteria are developed with reference to a safety case for the store or repository, for example they set standard data against which a radioactive waste package is assessed. A radioactive waste package is the wasteform with any overpack and the canisters (containers) into which the waste is emplaced for storage or disposal. A wasteform is the radioactive waste material and any encapsulating or stabilizing matrix in which it is incorporated. Generic requirements for wasteforms and packages were described by the International Atomic Energy Agency (IAEA) (1996, 1997). It has been emphasized however that the parameters of key importance for one particular waste management route may be different from another route and because of that the specific parameters have to be agreed on between bodies involved. Important properties are divided into those related to radioactivity, chemical and physical including mechanical and thermal properties. A summary of IAEA requirements is given in Table 8.1, Table 8.2, Table 8.3, Table 8.4, Table 8.5 and Table 8.6.

Given the variety of wastes and potential wasteforms, variations in local standards and regulations, environmental conditions and means of storage and disposal, the WAC developed by the IAEA are of necessity generic. Local regulators develop more specific WAC to meet the requirements of each situation. The choice of cement type and cementation technology depends on a number of factors, although WAC are among the most important. Required characteristics of cementitious wasteforms in Russia are given in Table 8.7. It specifies WAC requirements accordingly with the state standard GOST R 51 993-2002.

Cementitious Materials for Nuclear Waste Immobilization, First Edition. Rehab O. Abdel Rahman,
Ravil Z. Rakhimov, Nailia R. Rakhimova and Michael I. Ojovan.

Table 8.1 *IAEA generic WAC: wasteform*

Chemical and physical properties of the wasteform	
Input raw materials	Specifications for raw materials from R&D programme. Application of Quality Assurance and analysis (in-house or by the supplier) to ensure raw materials meet specifications. Direct measurement of properties or use of certified materials. Need to also understand the effect of age on materials and 'use by' date. Need to control storage conditions to prevent spoilage
Waste loading	Target waste loading derived from experimental research programme. Waste loading variation studies to define range of acceptable waste loading. Requires documented evidence to ensure compliance. Will require process control to ensure waste loading limits are not exceeded, possibly with testing
Chemical composition of the wasteform/waste	Chemical composition and acceptable variation ranges. Key analyses are also required for components of the waste that present additional, non-radioactive hazards, for example combustible/flammable liquids and solids, oxidizers, corrosives (also for plant and equipment life), explosive materials, toxic materials (e.g. Cd and Hg, these can require additional WAC), reactive materials, gas evolving materials or those capable of evolving gas, organics, asbestos, biological components, components that may require regulatory notification. Require systems to identify and if possible exclude such materials or if present the process renders them into a form that is suitable for disposal/storage
Density, porosity	Measurement of the density and porosity of the product or correlation of size and dimensions of container with development and commissioning test programme densities
Relevant properties of form during processing	Identify key properties of the wasteform as it is processed and control methodologies and measurement parameters of process equipment and inputs to ensure they are met
Permeability to water and permeability to gases	Density and porosity of the product, direct or indirect measurement of permeability, degree of interconnected porosity. For certain wasteforms, such as cement, the permeability of the material to liquids and/or gases is a key parameter
Homogeneity and compatibility of the waste with the matrix	Measured homogeneity of the product at the micro and macro scales either by direct measurement of the wasteform product or by utilizing data from a research/commission programme
Thermal stability	Calculated or measured radiogenic heat and modelling of storage/repository conditions to derive expected temperature profiles and heat evolution from the wasteform/package. Thermal tests on matrix stability at temperatures likely to be encountered under storage conditions or in the repository
The percentage of water incorporated, exudation of water under compressive stress, shrinkage and curing[a]	Applicable only to certain wasteforms, for example grouts and geopolymers. Direct measurement of wasteform or utilization of data from a test programme
The leachability/ corrosion rate of the wasteform	Measured short- and long-term leach tests. Quality Assurance tests such as Product Consistency Test under deionized water or other medium. Long-term tests to determine leaching mechanisms and develop models for behaviour of the wasteform/package under geological repository conditions

[a] These are related mainly to cement/grout materials.

Table 8.2 *IAEA generic WAC: container*

Chemical and physical properties of the container	
Container dimensions	Direct measurement and comparison with specifications
Materials of construction	Certified materials or direct testing
Porosity, permeability to water and permeability to gases. The characteristics of the lidding and sealing arrangements	Test data, for example leak tests, to measure such properties. Engineering design and testing of the container to ensure compliance with sealing criteria
Thermal conductivity	Test data on actual container material or reference to specifications for certified materials. Possible application of models to show heat evolution from the waste package
Container solubility and corrosion in corrosive atmospheres or liquids such as water or brines	Corrosion resistance of the container under storage and repository conditions. Measurement and modelling of behaviour of the container material either from test data or with the use of certified materials with known corrosion behaviour
Compatibility of container material with the wasteform	From R&D test data and reports

Table 8.3 *IAEA generic WAC: waste package*

Physical properties of the waste package	
Labelling of package for Quality Assurance purposes	Requires an appropriate Quality Assurance system, including records required for each package and records storage procedures. Labels with long-term life may require a test system. Need to also consider the retrievability of records over the storage lifetime
Package weight	Maximum weight specified for handling, transport and storage. In the case of fissile materials there may be a maximum weight associated with the amount of fissile materials per unit volume of the store
The number of voids in the container (which are to be minimized)	Drawings of the package including spaces and means of fixing the wasteform
Sensitivity to changes in temperature	Assumed to mean both thermal cycling that may be experienced during storage, for example, night–day, summer–winter, plus changes due to radiogenic heat. It may also include sensitivity to thermal conditions encountered in a repository. Can be done directly by testing response to thermal cycles or indirectly via modelling

Table 8.4 *IAEA generic WAC: wasteform and package, mechanical properties*

Mechanical properties of the wasteform and package	
The mechanical properties of the wasteform include its tensile strength, compressive strength and dimensional stability	Direct measurement of appropriate mechanical properties of the wasteform with possible application of mechanical models to determine the behaviour of the wasteform and package under load
The mechanical properties of the waste package include its behaviour under mechanical (static and impact) or thermal loads	Load bearing test on the waste package. Impact tests on waste package system, fire resistance, for transport, storage and disposition safety scenarios

Table 8.5 *IAEA generic WAC: wasteform and package, radiological properties*

Radiological properties of the wasteform and package	
Surface contamination	Maximum level for wasteform and package exiting from the process line and maximum level for contamination on overpack or flask. Determined by direct measurement of fixed (if possible) and non-fixed contamination
Radiation stability	Stability of the package to radiation damage it will experience over its lifetime. The package must retain sufficient stability to last through its period of storage. When disposed of under geological conditions, the key parameter is the effect of radiation damage on the ability of the wasteform/package to retain the long-lived radionuclides. Transmutation effects on the wasteform should also be considered
Dose rate	Dose rate at surface of package with target such that the dose not exceed regulatory limits. Requires limits for two safety scenarios: (1) handling during process and transport of individual packages; and (2) conditions in the storage facility where multiple packages are likely to be present. Note this varies depending on the store design, degree of shielding, how many packages are in the store, and whether and how often inspection is required

Table 8.6 *IAEA generic WAC: containment capability*

Containment capability of the waste package system	
The capability for the fixation and retention of radionuclides; and the diffusion and leaching of radionuclides in an aqueous medium	Leaching test for wasteform. Testing/assessment of waste package under geological conditions. Assessment of the release rates of key radionuclides from the package under repository conditions. Repository modelling of release scenarios. Interrelated compatibility of package materials, wasteform and repository materials
The release of gas and tritium under standard atmospheric conditions or the conditions in a repository	Measurement and calculation of potential gas generation and releases from the package
The water tightness and gas tightness of the package sealing device	Measurement of water and gas tightness of package under relevant safety scenarios for transport, storage and disposition

Table 8.7 Acceptance criteria for low and intermediate level radioactive waste cementitious wasteforms in the Russian Federation

Criterion	Limit	Testing method
Normalized leaching rate (by ^{137}Cs) [g/(cm^2 day)]	$<10^{-3}$	GOST 29114
Mechanical durability (compressive strength)[a] (MPa)	>4.9	GOST 310.4
Radiation durability (Gy)	10^6	Change of mechanical durability
Freeze durability (freeze–thaw cycles)	>30	GOST 10060.1
Durability to long-term water immersion (days)	90	Change of mechanical durability

[a] For comparison regulatory requirements on compressive strength of cementitious wasteform are as follows:

0.35 MPa in France;
3.4 MPa in the US;
5 MPa in Slovakia;
7 MPa in the UK;
10 MPa in Switzerland.

8.2 Role of Material Performance

Performance of cementitious materials including cementitious wasteforms in conditions of storage and disposal is of paramount importance. The role of the wasteform in long-term safety typically depends on repository design and facility location site. The repository designs rely on a multi-barrier approach, when each component of an engineered barrier system such as concrete vaults, concrete monoliths containing the waste packages immobilized by a cementitious grout, will contribute to the long-term safety. The role of the cementitious materials including the wasteform can be therefore very important in ensuring the overall safety of storage and disposal. The experience of cement utilization demonstrates its prominent long-term durability, for example modern Portland cements have been in use for approximately 150 years whereas $Ca(OH)_2$-based compositions have been successfully used in civil engineering for more than 2000 years (Glasser and Atkins 1994; Glasser 2002, 2011).

Safety assessment of radioactive waste disposal involves analyses of potential releases of radionuclides and subsequent transport into the human environment. An important stage of assessment is the identification and screening of all the features, events and processes (so-called FEPs) relevant to long-term safety. A feature is an object, structure or condition that has a potential to affect repository system performance. An event is a natural or human-caused phenomenon that has a potential to affect repository system performance and that occurs during an interval that is short compared with the period of performance. A process is a natural or human-caused phenomenon that has the potential to affect repository system performance and that occurs during all or a significant part of the period of performance. A comprehensive set of FEPs captures all of the phenomena that are potentially relevant to the long-term performance of a repository system. An international list of FEPs along with the basis for selecting the FEPs that should be included in safety assessment has been published (OECD/Nuclear Energy Agency, 2000). All of the important FEPs are then combined in scenarios which determine possible future states including undisturbed and disturbed (altered by disruptive events) states of the repository system. The performance assessment develops conceptual and mathematical models of the repository system that capture the coupled effects of all scenarios included FEPs.

Performance assessments of radioactive waste disposal systems are iterative processes involving site specific, prospective modelling evaluations of the post closure time phase. Performance assessments have two primary objectives: (1) to determine whether reasonable assurance of compliance with quantitative performance objectives for protection of human health can be demonstrated; and (2) to identify critical data, facility design and information needs and model development needs for defensible and cost-effective licensing decisions and developing and maintaining operating limits, such as WAC (Langton *et al.*, 2009).

The radionuclide source term is the most important part of safety assessment; therefore the radionuclide release modelling should be scientifically sound and include the long-term release rates of radionuclides from the radioactive wasteforms (Drace *et al.*, 2012). Radionuclide release rates are dependent on temperature and chemical parameters of water (moisture) in contact with wasteform. Performance assessment involves for simulation coupled thermo-hydro-mechanical (THM) models combined with reactive transport models. The reactions involved depend on the characteristics of the wasteforms, the radionuclides and their interaction with surrounding geologic materials. Coupled THM models are used to simulate the simultaneous flow of heat and water in deforming rocks or soils. These models have been applied to the safety assessment of radioactive waste repositories as well as in a number of other engineering fields. A number of THM computer codes have been developed such as TOUGH, FLAC3D, ROLG, EBSCOM, SPOMP, AREST-CT and STORM.

8.3 Expected Performance of Cements

Cementitious materials are essentially porous solids consisting of a complex mixture of crystalline and gel-like phases with an interstitial pore solution that is in chemical equilibrium with the solid phase. By their phase assemblage they are metastable, therefore they will change in a disposal environment with time releasing some of the waste radionuclides retained. Over a given period of performance, a cementitious monolith may be in contact with one or more forms of surrounding media such as rain and ground waters containing dissolved constituents, and atmospheric gases including water vapours and carbon dioxide. Figure 8.1a is a conceptual illustration of release processes, influential physical and chemical factors and interfacial phenomena that may exist for cementitious materials in the environment (Van der Sloot *et al.*, 2009). Figure 8.1b shows four stages of evolution of cements which have been identified in a chemical approach to cementitious material degradation under simple leaching conditions (Glasser, 2011):

Stage I. The pH is dominated by alkalis. All normal cement mineral hydrates are present.
Stage II. The pH is dominated by $Ca(OH)_2$. All normal hydrates are present.
Stage III. $Ca(OH)_2$ is consumed. Calcium silicate hydrate, depending on composition, pH is buffered in the range 10–12.
Stage IV. Only degradation and reaction products are left to condition pH.

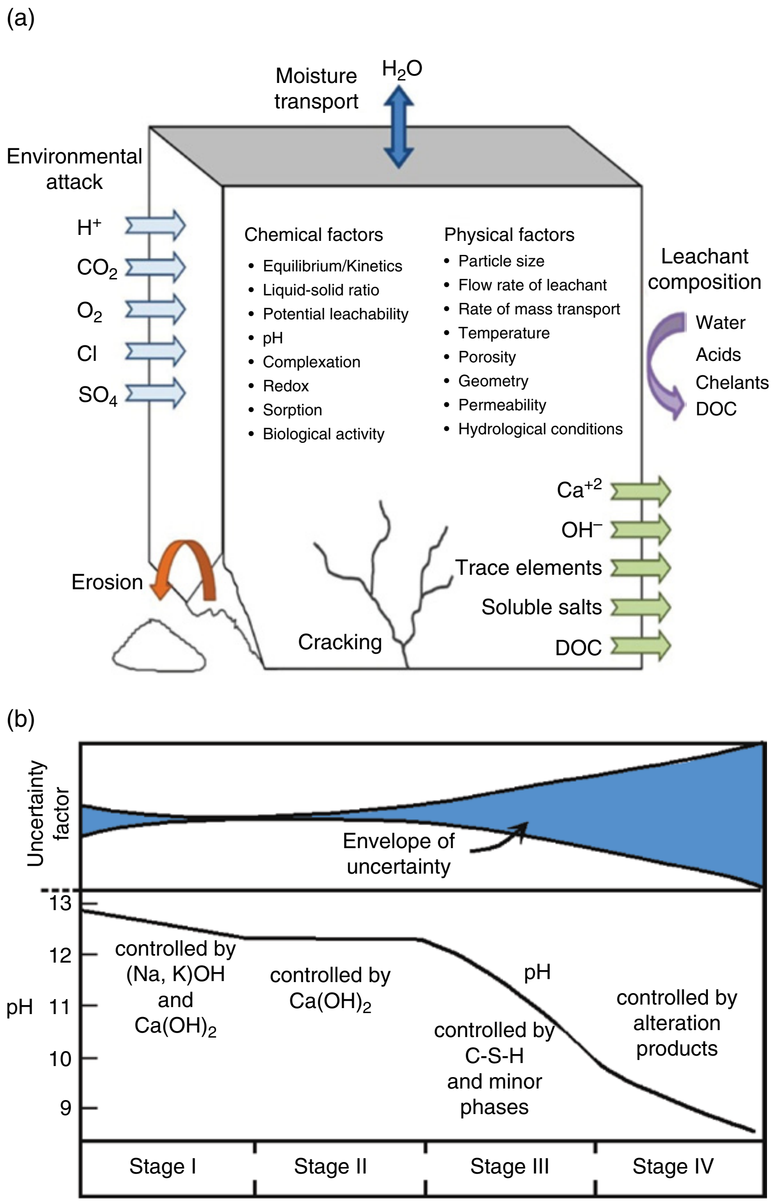

Figure 8.1 *(a) Internal factors and external phenomena that influence the leaching process in cementitious materials. DOC, dissolved organic carbon. (b) Evolution of cements in disposal environments and associated uncertainties. Reproduced from Glasser, 2011. With permission from Elsevier*

During Stage I the pH of pore water is dominated by alkali hydroxides and their coexistence with portlandite. Alkalis initially totalling approximately 1 wt% on an oxide basis in Portland cements are gradually lost from cement by leaching, which is initially diffusion-controlled; however, during this period the solubility of portlandite is greatly suppressed (Glasser, 2011). Stage II is characterized by a constant solid phase assemblage consisting of portlandite, calcium-saturated calcium silicate hydrate, AFm and AFt phases. A hydrated Portland cement contains about 20–25 wt% portlandite and thus a considerable reservoir of solid mass capable of conditioning pH is present. The pH and composition of the cement pore fluid is constant throughout Stage II as long as portlandite persists. Moreover the pH does not depend on the amount of portlandite but only on its presence (Glasser, 2011). During Stage III the most important phase controlling pH is calcium silicate hydrate which has a variable composition and hence a variable pH conditioning ability from high at Ca/Si ratios of approximately 1.5 and above to moderate ($pH = 10.5$) at Ca/Si ratios of approximately 1.0. The mass loss is typically balanced at least in part by mass gain of species such as sulphate and carbonate. Calculations can be made for specific compositions which however are difficult for realistic repositories with uncertainties which tend to accumulate with the progress of reaction (Figure 8.1). Stage IV is characterized by the final exhaustion of the phases originally present in cement and their partial to total replacement by alteration products. The nature and amount of alteration products is environment-specific and hence the envelope of uncertainty continues to expand in this stage.

Stage II is the most important corrosion stage of cementitious wasteforms as well as of cementitious materials used as engineered barriers (backfilling, construction). This phase is expected to last thousands to tens of thousands of years and is characteristic for all Portland cements used worldwide and is not much affected by the presence of waste or by the conditions of the local disposal environment.

Kinetically controlled diffusion processes also occur when cements react with liquids. Leaching caused by the percolation of water through a cured cement system is potentially important for nuclear waste management, and is dependent on the permeability of the system. Pure water leaches out hydroxides, dissolves CH (portlandite) and decomposes hydrated silicate and aluminate phases. Monosulphate was shown to decompose before ettringite confirming evidence that monosulphate decomposes below pH 11.6, while ettringite decomposes below pH 10.7 (Taylor, 1990). Diffusion processes are typically relevant for the release of mobile radionuclides such as ^{137}Cs and ^{90}Sr. Numerous leaching studies have shown that for a constant geometry calcium leaching is proportional to the square root of time for contacting water solutions approaching the composition of pure water (Glasser, 2011). Various standard leach tests express the extent of leaching in terms of diffusion coefficients.

Cementitious materials are sensitive to attack by some chemical species present in the waste and environment such as CO_2, chloride and sulphate which may lead to deterioration of their properties (Glasser *et al.*, 2008). For example, carbonation reactions can lead to decomposition of cement hydrates (e.g. portlandite), and to the subsequent formation of $CaCO_3$ or to the dissolution of calcium. These processes can ultimately lead to an increase in the porosity and water permeability and cause a loss of mechanical strength. Indeed the durability of cement depends largely on permeability, which in turn depends on the porosity of the system.

8.4 Wasteform Leaching Parameters

The most likely mechanism by which radionuclides may be removed from the wasteform is via the groundwater which may intrude into the repository once the engineered barriers including containers degrade. An important requirement for wasteform acceptance for storage and disposal is therefore the chemical durability which is expressed as a normalized leaching rate. It determines how well the radionuclides of concern are retained within the wasteform in a wet environment. Estimating the rate of leaching from a wasteform during disposal is a key consideration in assessing an immobilization method. Low matrix solubility means reduced likelihood of radionuclide release therefore the leaching behaviour of cemented radioactive waste is important to ultimately ensure the overall safety of storage and disposal systems.

The leaching behaviour of wasteforms containing different amounts of waste radionuclides is compared using the normalized leaching rates NR_i for each *i*th nuclide expressed in g/(cm^2 day) and the normalized mass losses NL_i, expressed in g/cm^2. These are determined using a range of approved tests such as the IAEA test protocol (Hespe, 1971) and ISO 6961-1982 via measuring concentrations c_i (g/l) or activities a_i (Bq/l) of nuclides in the water solution contacting the wasteform after a time interval t expressed in days. The mass fraction of a given nuclide i in a wasteform is defined as:

$$f_i = \frac{w_i}{w_0}, \tag{8.1}$$

where w_i is the mass of nuclide in the wasteform (g) and w_0 is the mass of the wasteform (g). The specific content of a given radionuclide in a wasteform q_i (Bq/g) is defined as:

$$q_i = \frac{A_i}{w_0}, \tag{8.2}$$

where A_i is the radioactivity of radionuclides in the wasteform (Bq). The average normalized leaching rate of non-radioactive nuclides NR_i [g/(cm^2 day)] is calculated using the expression:

$$\mathrm{NR}_i = \frac{c_i V}{f_i S t} \tag{8.3}$$

where S is the surface area of the waste form in contact with the water (cm^2), V is the water solution volume (l) and t is the test duration in days. The average normalized leaching rate of radioactive nuclides NR_i [g/(cm^2 day)] is calculated using the expression:

$$\mathrm{NR}_i = \frac{a_i V}{q_i S t}, \tag{8.4}$$

where a_i (Bq/l) is the specific radioactivity of solution. The normalized leaching rate is often measured in cm/day, simply dividing the NR_i [g/(cm^2 day)] by the density of material in g/cm^3.

Normalized mass losses NL_i (g/cm^2) are determined for non-radioactive and radioactive nuclides, respectively, from the following equations:

$$\mathrm{NL}_i = \frac{c_i V}{f_i S}, \tag{8.5a}$$

and

$$\mathrm{NL}_i = \frac{a_i V}{q_i S} \tag{8.5b}$$

Real (not normalized) radionuclide leaching rates R_i [Bq/(cm^2 day)] can be determined by multiplying normalized leaching rates NR_i by the specific radionuclide content in the wasteform q_i (Bq/g):

$$R_i = \mathrm{NR}_i q_i \tag{8.6}$$

Correspondingly the real losses of radionuclides per unit of contacting surface (Bq/cm^2) are given by:

$$L_i = \mathrm{NL}_i q_i \tag{8.7}$$

The higher the normalized leaching rates NR_i and specific radioactivity of waste q_i the higher the leaching rates R_i. Higher q_i waste requires either a more durable wasteform or an additional package to diminish the overall potential losses.

Normalized leaching rates are determined via laboratory and field tests. Laboratory tests can be either relatively short-term accelerated tests aiming to sort samples and study the effects of variables or longer term aiming to simulate the actual conditions in a disposal environment.

8.5 Laboratory Tests

Many of the standard tests procedures for radioactive wasteforms are applicable to cementitious materials. These can be grouped into (A) static, (B) semi-static and (C) dynamic tests, depending on whether the water solution in contact with the wasteform is static or refreshed either intermittently or continuously during the test (Ebert and Fuhrmann 2010; Van Iseghem, 2012):

A. IAEA/ISO 6961-82 (1982) and ASTM C1220-98 (2004) (MCC-1). Static tests, which expose a monolithic sample to demineralized (or another reference) water. The results of the test are expressed as normalized or total mass losses, or saturation concentrations in the solution of particular elements.
B. ANSI/ANS 16.1 (ANS, 2009). Semi-static test, which exposes a monolithic sample to demineralized water with a total replacement of the solution after specified intervals (hours to days). The results are expressed in terms of a leachability index (LI) or a diffusion coefficient.
C. ASTM C1662-10 (2010) and ISO 16797-04 (2004). Dynamic tests, which expose a monolithic or crushed sample to continuously flowing water. The results are expressed as normalized mass losses or a dissolution rate.

Table 8.8 Parameters used in testing nuclear wasteforms

Test	Temperature (°C)	S/V (cm^{-1})	Renewal of solution	Duration (days)
IAEA	25 ± 5	≤0.1	Daily 1 week, weekly 8 weeks, monthly 6 months, twice yearly	Unlimited
ISO 6961-82	40, 70, 100 ± 1	0.1–0.2	Daily 5 days, twice second week, weekly 4 weeks, monthly later	Unlimited
ASTM C1220-98 (MCC-1)	40, 70, 90	0.1	No renewal	3, 14, 28
ANSI/ANS 16.1	17.5–27.5	0.1	2, 7, 24 h, daily 4 days, after 14, 28, 43 days	90
GOST-29114-91	25, 40, 90	0.1–0.3	Daily 3 days, after 7 days weekly, then monthly	28 and longer

The experimental variables are temperature (T, °C), flow rate (F, cm^3/s), sample surface area (S, cm^2) to water solution volume (V, l) and the composition of the solution (g/cm^3). The standard test procedures mentioned above are widely used for wasteforms such as cementitious materials and glasses. Table 8.8 summarizes the conditions used in test protocols.

The ANSI/ANS 16.1 test protocol determines the effective diffusivity and surface release of constituents (including radioactive species) in a monolithic wasteform. This standard provides a uniform procedure to measure and index the release of radionuclides from wasteforms as a result of leaching in demineralized water for 5 days or longer. The ANS/ANSI 16.1 test has much in common with the original IAEA test (Hespe, 1971). A schematic of the test is shown in Figure 8.2.

The ANSI/ANS 16.1 test protocol provides the so-called LI index of the wasteform. The LI is calculated from a series of immersions in water. The leachant volume V is 10 times the surface area of the sample S (S/V = 0.1). The effective diffusivity D (cm^2/s) is calculated using the equation (Russell *et al.*, 2006):

$$D = \pi \left[\frac{V}{S} \frac{c_n}{w t_n} \right]^2 t_L, \tag{8.8}$$

where V is the volume of specimen (cm^3), S is the geometric surface area of the specimen as calculated from measured dimensions (cm^2), w is the total quantity of a given element in the specimen at the beginning of the first leaching (g), t_n is the duration of the nth leaching interval (s), c_n is the quantity of a given element released from the specimen during the leaching interval n (g), t_L is the leaching time representing the 'mean time' of the leaching interval (s). Typical diffusion coefficients of cementitious wasteforms are of the order of 10^{-7}–10^{-5} cm^2/day, for example 10^{-12}–10^{-10} cm^2/s.

The LI of the wasteforms is then calculated according to the following equation:

$$\mathrm{LI} = -\log\left(\frac{D}{\mathrm{cm}^2/\mathrm{s}} \right) \tag{8.9}$$

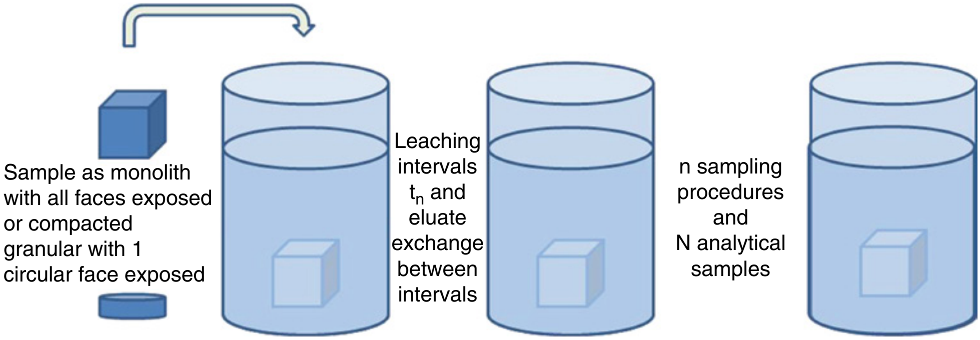

Figure 8.2 *Schematic of ANSI/ANS 16.1 test protocol procedures*

The lower the effective diffusivity the higher the LI meaning the better is the retention of radionuclides in a given wasteform. Typical LIs of cementitious wasteforms are of the order of 10–12.

The main purpose of laboratory tests is to qualify or benchmark the chemical durability of the cemented waste, and to identify values of specific parameters needed for modelling or safety evaluations of the disposal systems (Van Iseghem, 2012). The real behaviour of materials in a disposal environment is in many cases quite different from that in laboratory tests as laboratory test procedures are not realistic for conditions expected in a disposal environment. For example increased temperatures used to accelerate wasteform corrosion, pure (deionized) water and flow rates of the order of approximately cm^3/s are unexpected for disposal systems. Moreover small-sized and sometimes even finely crushed material does not represent real morphology of monolithic void-free wasteforms. Typical laboratory experiments lasting up to months cannot provide insight into the corrosion processes over hundreds to thousands of years. There is a need therefore for field tests of wasteforms in conditions similar to that expected in a storage/disposal environment.

8.6 Long-Term Field Tests

The evolution of the properties of cementitious materials in a repository is often extrapolated from conventional laboratory timescales to periods more typical of geological processes. The validity of the models used for such extrapolation can be tested by comparison of such predictions with observations of analogous geological or archaeological samples (McKinley and Alexander, 1992). A review of the archaeological analogue approaches to predict the long-term corrosion behaviour of carbon steel overpack and reinforced concrete structures in the French disposal systems was given recently by Neff *et al.* (2010). The test protocol ASTM C1174 (1991) covers the steps for the development of methods to aid in the prediction of the long-term behaviour of waste package materials and wasteforms in geological disposal conditions although no standard test procedures exist to evaluate the performance of cemented waste in real disposal conditions. Moreover, no single test would probably be sufficient to project long-term durability under the complex conditions of a disposal site (Van Iseghem, 2012). Nevertheless processes which control the long-term corrosion have to be known and understood in order to establish a predictive model for behaviour of wasteforms in a repository.

Field tests exposing cementitious wasteforms to environments similar to disposal conditions might result in quite different data compared with laboratory testing. A much smaller weathering and release rate is typical compared with laboratory data mainly because of processes which occur differently in field tests. The normalized leaching rate for the main waste radionuclide ^{137}Cs is as low as $1.7{\times}10^{-6}$ g/(cm^2 day) (Ojovan *et al.*, 2011) which is at the level of some glasses and ceramics for laboratory test conditions. The leaching rates for ^{60}Co are also low at a level of $(4.2–7.3){\times}10^{-5}$ cm/day (Plecas *et al.*, 2004). Various factors may be responsible for an increased apparent durability of wasteforms in field conditions such as groundwater composition, temperature and groundwater flow rate changes, as well as transport limitations and interactions between cements and clay (Sneyers *et al.*, 2001; Ojovan *et al.*, 2011).

In the USA a Cementitious Barriers Partnership Project (CBP) has been established by the US Department of Energy to develop a reasonable and credible set of tools to improve understanding and prediction of the structural, hydraulic and chemical performance of cementitious barriers used in nuclear applications (Langton *et al.*, 2010). The CBP has defined a set of reference cases to provide a basis for experiments and model validation, and for improving conceptual models and reducing model uncertainties. These reference cases include two reference disposal units and a reference storage unit:

- a cementitious low activity waste form in a reinforced concrete disposal vault;
- a concrete vault containing a steel high-level waste tank filled with grout (closed high-level waste tank);
- a spent nuclear fuel basin during operation.

Each case provides a different set of desired performance characteristics and interfaces between materials and with the environment. Field tests of cementitious wasteform carried out in near surface conditions can be used as a reference for near surface disposal of wastes. The performance of solidified radioactive wastes has been studied at Moscow SIA ‘Radon’ for several decades (Dmitriev *et al.*, 2005). The focus of this study is to analyse the long-term behaviour of radioactive wastes immobilized in glasses, bituminous materials and cements in near surface type repositories. The research programme comprises investigation of bore-hole, shallow ground and mound type repositories. Here data on field tests of cementitious materials are given for mound type and shallow-ground (vault) repositories.

8.6.1 Mound Type Repository Field Tests

The mound type repository is one of the simplest near surface type repositories without additional engineered barriers and is used among others for disposal of low-level radioactive wastes. Long-term field experiments of cemented radioactive wastes in the mound type repository were initiated in 1965. Cemented radioactive wastes in the form of 73 cubic blocks of sizes 30 × 30 × 30 cm were disposed of in a mound type repository. A schematic is shown in Figure 8.3a and a photograph taken in 2004 is shown in Figure 8.3b. The cemented blocks were located in the repository on a concrete plate inside steel trays. The blocks were covered by a 0.2 m thick layer of sand and gravel, a 0.5–0.7 m thick layer of loam and then a 0.1–0.3 m thick layer of sod.

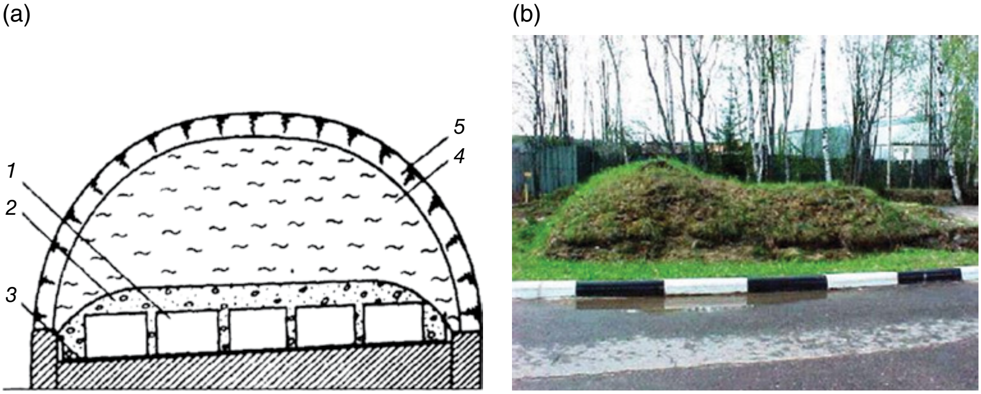

Figure 8.3 (a) Schematic of mound type repository. 1, Wasteform blocks; 2, sand layer; 3, steel tray; 4, sod layer; 5, loam layer. (b) Photograph of repository in summer 2004. Reproduced from Glasser, 2011. With permission from Elsevier

Table 8.9 Characteristics of testing site: Climate

Climatic characteristics of testing site				
Parameter/Season	Winter	Spring	Summer	Autumn
Average temperature (°C)	−5.77	8.14	18.52	5.16
Average precipitation (mm)	134	90	175	158

Table 8.10 Characteristics of testing site: rock

Burial site host rock parameters	
Annual average soil temperature (°C)	4.5
Depth of seasonal freezing (m)	0.7
Content of clay particles (wt%)	Up to 30
Specific weight of soil (g/cm^3)	2.5–2.7
Volume density (g/cm^3)	1.9–2.4
Moisture (wt.%)	20–30
Ionic-exchange complex	Ca^{2+}, Na^+, Mg^{2+}, K^+
Ion-exchange capacity (mg eq./100 g soil)	25–39
Distribution coefficient for ^{137}Cs (ml/g)	2000
Distribution coefficient for ^{90}Sr (ml/g)	300
Coefficient of filtration of coat loam layer (cm/day)	0.3–0.8

Testing conditions of the experimental burial site are given in Table 8.9, Table 8.10 and Table 8.11. Data on groundwater composition from the burial site, averaged for four control boreholes, are given in Table 8.12. The test conditions may be considered as water-saturated. Note that although in many instances unsaturated conditions are expected to prevail in real repository systems, saturated conditions are often specific for a long period of time.

Table 8.11 *Characteristics of testing site: minerals*

Burial site host rock compositions (wt%)							
Mineral	Quartz	Microcline	Albite	Illite	Smectite	Calcite	Dolomite
Soil	76.9	10.8	4.9	2.7	2.6	1.2	0.8
Sand	83.3	4.6	7.6	1.5	1.2	1.8	2.1

Table 8.12 *Characteristics of site groundwater (mg/l)*

Salt content	Fe^{3+}	Ca^{2+}	Mg^{2+2}	Na^+	K^+	Cl^-	NO_3^-	HCO_3^-	CO_3^{2-}	SO_4^{2-}
292.47	1.16	48.74	20.91	13.11	1.26	13.17	2.30	258.03	12.57	4.73
pH	Average 7.6–7.7									

Table 8.13 *Composition of atmospheric precipitates (mg/l)*

pH	Salt content	Na^+	K^+	Ca^{2+}	Mg^{2+}	Fe	Cl^-	NO_3^-	HCO_3^-	SO_4^{2-}	SiO_2	B
6.89	31.56	0.32	1.25	4.67	2.28	0.4	1.25	2.17	29.77	3.71	0.48	1.4

Meteorological observations on the site showed an average temperature of 6.5°C and 557 mm of precipitation per year. The dominant wind direction was SE–S–SW. The atmospheric precipitate composition is given in Table 8.13.

The water which was in contact with cementitious wasteforms was periodically collected and analysed. Water sampling was performed periodically, usually twice a month (except in winter). The volume of water v_j (l) was recorded at each sampling time. Water aliquots were retained for analysis. Standard radiometrical technique was applied including measurement of the specific radioactivity of water samples a_j (Bq/l). Overall measurement errors were not higher than 10%.

Atmospheric waters (rainwater and melted snow) which infiltrated through the repository covering layers and were in contact with the cement blocks were collected and analysed for the content of radionuclides from 1965 to 1968. It has been found that with time the amount of water has diminished. This diminution was explained by the natural thickening (densification) of covering clayey layers above the cemented blocks. The volume of groundwater, $V(t)$, collected over time t, was calculated as a sum of the volume of the individual batches (v_j) collected. The amount of radionuclides leached from the cementitious wasteform $A(t)$ (Bq) was calculated using:

$$A(t) = \sum_j a_j v_j \tag{8.10}$$

The normalized mass loss of radionuclides, NL (g/cm^2), was obtained from:

$$\mathrm{NL} = \frac{A(t)}{qS}, \tag{8.11}$$

where S (cm^2) is the cementitious wasteform–water contact surface area and q (Bq/g) is the specific radioactivity of wasteform. The average normalized leaching rate, NR (g/cm^{2}day), was then calculated using:

$$\mathrm{NR} = \frac{\mathrm{NL}}{t} \tag{8.12}$$

where t is the test duration in days. The dimensionless leached fraction of radionuclides (also termed the cumulative leached fraction), CLF(t), from the wasteform was calculated using:

$$\mathrm{CLF}(t) = \frac{A(t)}{A(0)} \tag{8.13}$$

where $A(0)$ is the initial level of radioactivity (total radioactivity in Bq) of the wasteform. Depending on the dominant leaching mechanism the CLF can be expressed as (Drace *et al.*, 2012 and Section 9.3):

$$\mathrm{CLF}(t) = Q_0[1 - \exp(-kt)] \tag{8.14}$$

for the surface dissolution mechanism (also termed instantaneous surface dissolution), where k is the surface reaction rate constant and Q_0 is the fraction of radionuclides on the surface;

$$\mathrm{CLF}(t) = 2\left(\frac{S}{V}\right)\sqrt{\frac{Dt}{\pi}} \tag{8.15}$$

for the diffusion controlled mechanism, where D is the effective diffusion coefficient;

$$\mathrm{CLF}(t) = \left(\frac{S}{V}\right)U_0 t \tag{8.16}$$

for constant dissolution of the block, where U_0 is the dissolution rate.

The experiments with mound type repository have shown that leaching of radionuclides occurs at the highest rate during the initial period of contact with groundwater. In 1966 radiometry of contacted water showed that the total amount of radionuclides leached from blocks was A(1966) = 0.149 MBq which gave CLF(1966) = 0.0200% (or 200×10^{-6}), whereas in 1968 radiometry of contacted waters showed that the total leached radioactivity was A(1968) = 2.1 kBq which gave CLF(1968) = 0.0212% (or 212×10^{-6}).

In 2004 the mound type repository was opened for retrieval of cemented waste. Samples of soil and cemented blocks were taken for analyses. Visual inspection does not identify damaged blocks with chips. As seen in Figure 8.4, after 39 years of storage the cement blocks are preserved in an excellent physical condition. Mechanical damage of cementitious materials is typically caused by freeze–thaw cycles and is due to overpressure in pore space filled by water, for example freeze–thaw of free or capillary water. The mound type repository partly smooths the amplitude of such cycles but cannot exclude them because of the small thickness of covering materials. Hence, the preservation of the cement blocks is due basically to the inherent high durability of the cementitious wasteform (Sobolev *et al.*, 2005).

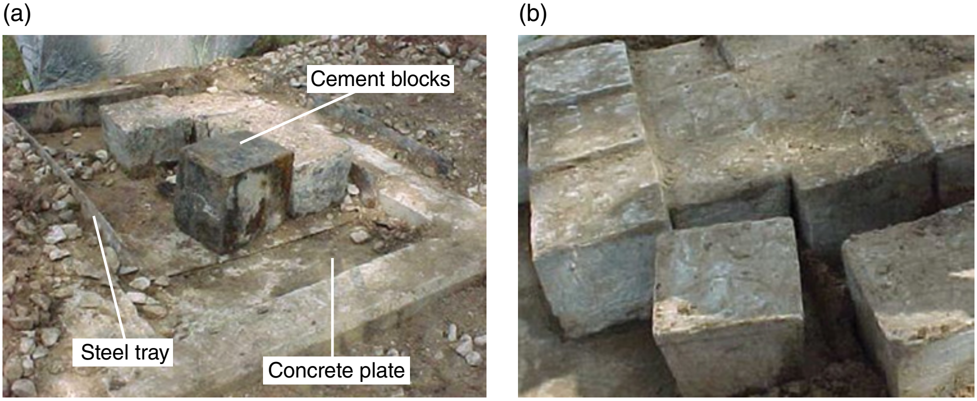

Figure 8.4 *Blocks of cemented aqueous radioactive waste after 40 years of burial in a mound type repository. Reproduced from Glasser, 2011. With permission from Elsevier*

Table 8.14 *Properties of cementitious wasteforms retrieved*

Mechanical strength (MPa)	4.9–20
Moisture (%)	3.3–6.0
Porosity (%)	17.3–32.3
Density (g/cm^3)	2.4–2.8
Main phases	Calcium silicate hydrate, calcite, ettringite, portlandite, alite
Normalized leaching rate (total β by ^{137}Cs), laboratory tests [g/(cm^2 day)]	7.3×10^{-6}–4.7×10^{-4}

Samples of cemented radioactive wastes were analysed for physical and chemical properties. Data obtained on retrieved cement blocks are given in Table 8.14. Mechanical strength of cemented radioactive waste in the range from 5.1 to 10.2 MPa complies with national requirements for cemented radioactive wastes. Normalized leaching rates of cement samples were measured using IAEA test protocol (Hespe, 1971). The rates were obtained from laboratory tests using specimens taken from the retrieved blocks. The results obtained (Table 8.14) are in the typical range for cemented radioactive wastes.

The radiometry of cemented waste demonstrates that accounting for the natural decay the inventory of radionuclides remained unchanged, for example the leached inventory is extremely small and is within the measurement errors. Moreover, no notable impact was identified on the near-field zone of cemented waste. Low leaching rate along with good mechanical strength of the cemented blocks after 39 year of storage in the mound type repository confirms reported results on the low ecological hazard of cemented radioactive wastes.

In summary, investigations of old cemented wastes from mound type repositories show that cement compounds can keep their immobilizing properties for a long time provided that the protective barriers capable of eliminating or reducing to a minimum the effect of natural destructive factors on the wastes, such as filtering precipitations and freeze–thaw cycles, function properly.

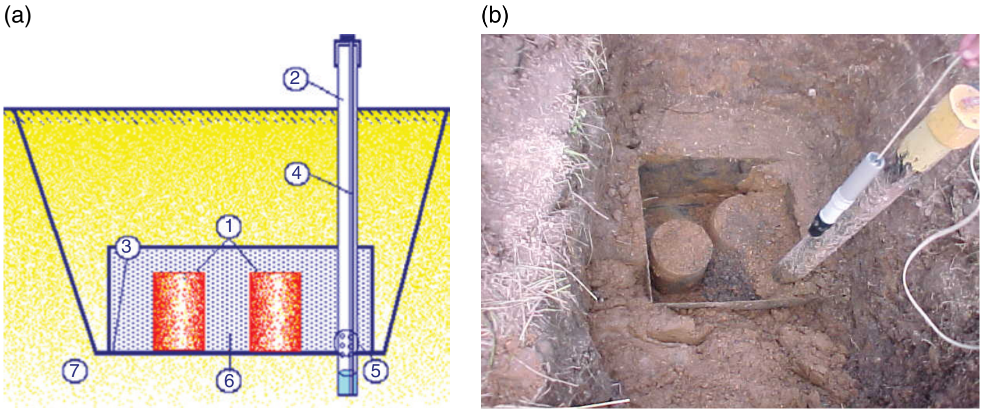

Figure 8.5 *(a) Schematic of mound type repository. 1, Wasteform blocks; 2, water trap; 3, steel tray; 4, sampling pipe; 5, perforation; 6, backfill sand; 7, host rock. (b) Photograph of opened repository in July 1999 (after 12 years)*

8.6.2 Vault Repository Field Tests

Cementitious wasteforms in the form of three cylindrical samples ($\varnothing = h = 24$ cm) were placed for long-term testing in a shallow-ground repository. Stainless steel trays holding cementitious wasteforms were placed at a depth of 1.7 m which is below the soil's freezing depth (0.7 m). Pure coarse sand was used to backfill the cemented blocks in the tray to facilitate infiltration of water to the blocks and to isolate them from direct contact with the host rock. The space outside the containers was filled with host loamy soil from the land surface. The stainless steel tray was supplied with a water trap and a tube for water extraction by pumping (Figure 8.5).

Cementitious wasteform samples for field test in the vault type repository were prepared in the form of cylinders using the technological procedures and equipment used on cementation of radioactive waste (Ojovan and Lee, 2005). The parameters of the wasteforms prepared are given in Table 8.15. Portland cement type Russian designation M-500 was used. The aqueous waste to cement ratio was 0.6 and the water to cement ratio ratio was 0.43 (on wt% basis). Calculated waste loading of the final product was 37.5 wt%.

A(0) = 92.4 MBq was the initial level of radioactivity in the K-28 cementitious wasteform. Data on the volume and specific radioactivities of the groundwater batches that had been in contact with the cementitious wasteform are shown in Table 8.16.

Table 8.17 gives data characterizing the retention properties of cementitious wasteforms in field conditions.

The repository was opened in July 1999, after 12 years, to examine the physical condition of the wasteforms, to obtain information on their alteration and to evaluate the nature, extent and distribution of radionuclide contamination within the environment closest to the wasteform (Figure 8.5b). The 12 year field test has demonstrated the ability of the cement matrix to provide a high degree of containment for short-lived radionuclides (^{137,134}Cs) under shallow-ground repository conditions (Ojovan *et al.*, 2011).

Better retention of radionuclides by cementitious wasteforms has been demonstrated by field tests at Oak Ridge and Argonne National Laboratories in the USA (Van der Sloot

Table 8.15 Characterization of wasteform samples used for long-term field tests

Sample	Weight (kg)	Contact surface, *S* (cm^2)	Waste loading (wt%)	Density (g/cm^3)	Specific radioactivity, *q* (kBq/g)
K-28	44.0[a]	5430	37.5	1.5	2.10

[a] Total weight of three cylindrical samples (Ø=*h* = 24 cm).

Table 8.16 Radioactive contamination of groundwater in contact with the K-28 cementitious wasteform

Average annual specific radioactivity of groundwater, Bq/l, (for the *n*th year of exposure)					
1	2	6	10	11	12
65.8	43.1	26.7	25.3	24.8	24.9
The total amount of groundwater was *V*(12 years) = 1747 l					

Table 8.17 Leaching properties of the cementitious wasteform K-28 in field conditions

NR [g/(cm^2 day)] (for the *n*th year of exposure)						CLF	
1	2	6	10	11	12	First year	Total
4.8×10^{-6}	3.1×10^{-6}	1.9×10^{-6}	1.8×10^{-6}	1.8×10^{-6}	1.7×10^{-6}	10^{-4}	4×10^{-4}

CLF, cumulative leached fraction; NR, average normalized leaching rate.

et al., 2009). Comparison of lysimeter leaching with standard leach test results of cementitious wasteforms indicated that lysimeter releases of ^{90}Sr were at least 100 times lower than leach tests, while for ^{137}Cs releases were five orders of magnitude less. These differences include limited contact with percolating water as well as retention of radionuclides on the soil of the lysimeters. The retained radionuclides remained bound to soil within the first 10–20 cm under the wasteforms.

8.7 Effect of Radiation

An additional factor which could potentially have an effect on cementitious wasteforms and radionuclide leach rates is self-irradiation of samples due to natural decay of waste radionuclides. Calculations have shown that the overpressure of radiolysis gases in cements is very limited and for intermediate-level waste can be of the order of 10 Pa if the specific concentration of ^{137}Cs is approximately 10^{-3} Ci/l (Chemeris *et al.*, 1999; Bouniol and Bjergbakke, 2008). The effects of gamma irradiation (^{60}Co) were studied using non-radioactive cementitious wasteform samples after a hardening period of 1 year (Ojovan *et al.*, 2011). The cumulative dose used was 10^6 Gy for all samples irradiated which is expected to be not higher than the waste lifetime absorbed radiation dose. The dose rate applied did not induce a significant temperature rise in the sample and the

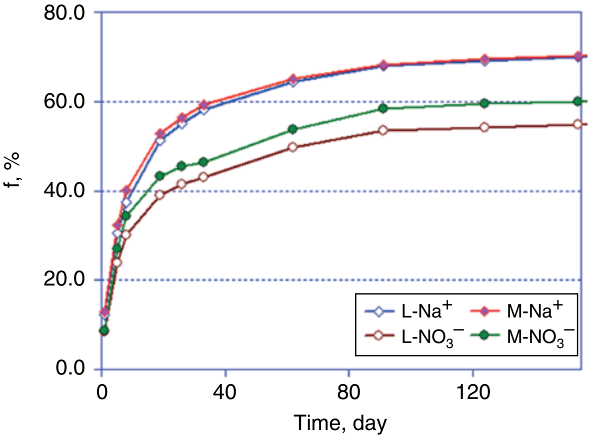

Figure 8.6 *Cumulative leached fractions of Na$^+$ and NO$_3^-$ measured in the laboratory leach test of non-radioactive cementitious wasteform samples subjected (L) and not subjected (M) to ^{60}Co gamma irradiation. The cumulative dose was 10^6 Gy*

radiolysis hydrogen production rate was low enough so that it did not cause any damage to the samples able to result in experimental artifacts. The average of duplicate test results for non-radioactive samples irradiated and non-irradiated are shown in Figure 8.6.

Differences in the leaching behaviour of irradiated and non-irradiated samples are insignificant. Although for 154 days of leaching test the CLFs of Na$^+$ and NO$_3^-$ were several per cent less in the case of irradiated samples, the leach rates at the later stages were essentially the same: for Ca^{2+}, Na$^+$ and NO$_3^-$ [in g/(cm^2 day)] 6.3×10^{-7}, 2.1×10^{-5}, 1.5×10^{-5}, and 8.9×10^{-7}, 2.1×10^{-5}, 1.4×10^{-5}, respectively, for the irradiated and non-irradiated samples.

8.8 Biological Effects

Biocorrosion of cementitious wasteforms is poorly investigated although it can potentially play an important role in the degradation processes of cementitious materials pre-sent in a disposal facility. Biologically driven destructive effects can be caused by both microorganism activities and the products of their metabolism such as acids, bases, ferments and other aggressive media. Microbiological examination of aged cementitious wasteforms extracted from a mound type repository have shown the presence of viable bacteria of different physiological groups such as denitrificating, fermenting, iron oxidizing and microscopic mushrooms (Varlakova *et al.*, 2009) which are potentially strong destructors of silicate minerals. Recent studies of cementitious wasteforms containing immobilized nuclear power plant operational radioactive waste under a long-term field test conducted from 1987 to 2007 confirmed the presence of microbiological species and activities due to their presence (Varlakova *et al.*, 2011). Microbiological species of several metabolic groups were identified within cementitious wasteforms, in the clayey soil near the wasteforms and in the groundwater in an experimental near-surface repository (Figure 8.7). The most populated medium was the soil with population density up to 3.6×10^5 colony/g. Microbial populations of generic type *Bacillus, Pseudomonas, Rhodococcus, Alcaligenes, Micrococcus, Mycobacterium* and *Arthrobacter* were identified on the cementitious

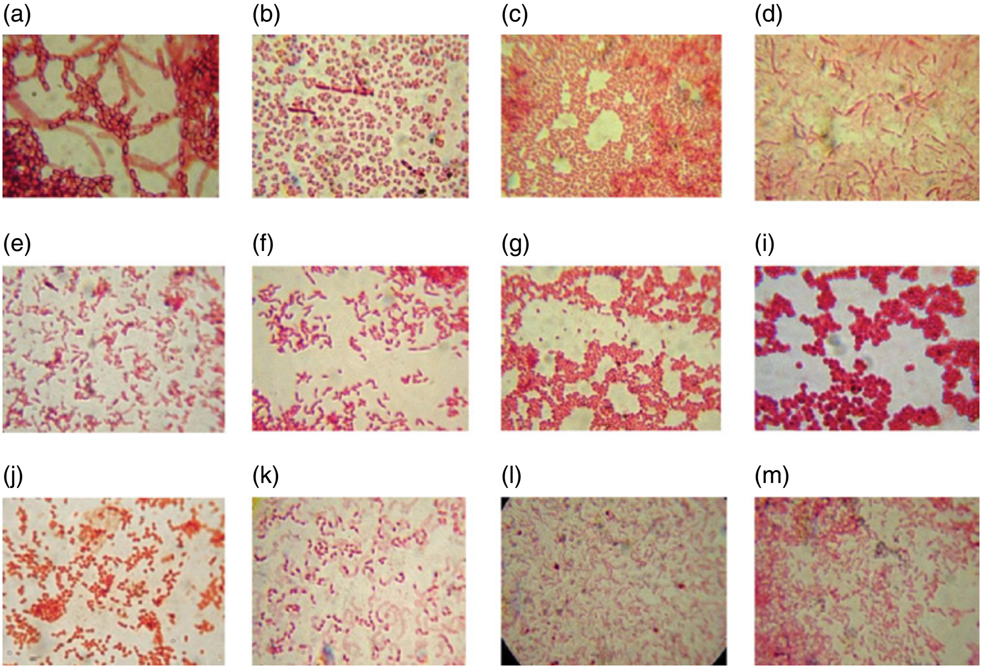

Figure 8.7 *Light microscopy microphotographs of bacteria (magnification ×1500). Rods and cocci belong to the families: (a, b)* Bacillus*; (c, d)* Pseudomonas*; (e)* Rhodococcus*; (f)* Mycobacterium*; (g, h)* Micrococcus*; (i, j)* Arthrobacter*; (k)* Alcaligenes*; (l)* Flavobacterium

wasteforms. Microbial populations of generic type *Bacillus, Pseudomonas* and *Micrococcus* were identified in the clayey soil near the cementitious wasteforms. Populations of *Arthrobacter, Pseudomonas, Alcaligenes, Rhodococcus, Bacillus* and *Flavobacterium* were identified in the groundwater contacting the cementitious wasteforms.

Both iron-reducing and iron-oxidizing bacteria were identified within the cementitious wasteforms. The most populated group was of the fermenting type which was present also in the cementitious wasteforms and in the water. The least populated group was of the sulphur-reducing type with densities of 2 colony/g in the wasteforms and 1 colony/g in the soil. The denitrating group was found in groundwater and soil whereas the nitrating group was found only in the soil. The microbiological species identified are potential destructors of silicate minerals including those present in cementitious wasteforms and containers. It has been concluded that as their population and activity can significantly increase with time they require careful consideration for long-term performance analysis.

8.9 Role of Filling Materials

Ordinary Portland cement (OPC) is the most common type of cement used for immobilizing liquid and wet solid wastes worldwide. Several Portland cement-based mixtures are currently used to improve the characteristics of wasteforms and overcome the incompatibility problems

Table 8.18 *Modified Portland cements and their use in waste immobilization*

Type	Additive	Waste stream	Additive function
Masonry cement	Lime	Containing boric acid	Adjusts pH
Portland sodium silicate cement	Sodium silicate	Organic liquids	Accelerates set, reduces porosity
Portland pozzolanic cement	Reactive silica	Containing sulphates	Reacts with $Ca(OH)_2$, reduces porosity
Portland BFS cement	Slag	Containing sulphates	Reacts with $Ca(OH)_2$ Latently hydraulic

associated with the chemical composition of certain types of radioactive waste. The addition of supplementary cementitious materials (SCMs), such as blast furnace slag (BFS) or pulverized fuel ash (PFA), which also react with the cement, increases the durability of material. For example, the addition of BFS decreases the permeability of the cement system, providing the BFS has reacted sufficiently to contribute to the matrix. The addition of supplementary SCMs can improve these properties. The addition of BFS or PFA has been found to significantly alter the porosity and pore distribution within the cement matrix. Kumar and Roy (1986) showed that BFS additions changed the pore size distribution towards smaller capillary porosity which had a direct effect on the permeability and diffusivity of ions, reducing both. Chloride ion diffusion through a 65% BFS: 35% OPC composite cement cured for 365 days was 1.5 orders of magnitude lower than diffusion though a neat OPC paste. After 28 days the difference in porosity was approximately 10%. These finding were confirmed by Detwiler *et al.* (1994) who found that voids left by the hydrating BFS formed a porous paste. These pores however were not expected to contribute to permeability because they were isolated from other pores in the material. Replacement levels of 30% were found to be equally effective in concrete cured at 70°C as those cured at ambient temperatures (Detwiler *et al.*, 1994). The presence of $BaSO_4$ has also been found to decrease the permeability of chloride ions in hardened mortars by forming large amounts of Friedel's salt ($C_3A–CaCl_2–10H_2O$), removing mobile chloride ions from the pore solution. Furthermore, by using such high replacement levels of cement by BFS a decrease in the heat evolved during initial hydration was reported due to a dilution effect (Escalante-Garcia and Sharp, 2000).

Modified or composite cements are used to immobilize waste containing specific components and contaminants (Ojovan and Lee, 2005). Table 8.18 gives data on modified Portland cements, additives and waste streams for which they are used.

OPC-based mixtures are currently used to improve the characteristics of wasteforms and overcome the incompatibility problems associated with the chemical composition of certain types of radioactive waste. In addition to cost reduction and energy saving, composite cements typically demonstrate superior long-term performance (Glasser, 2011; IAEA, 2013).

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9

Performance Assessment

During the early days of the nuclear era, the effort was focused on the development of nuclear reactor technologies. The realization of the importance of long-term safe radioactive waste management was not considered a significant problem (Abdel Rahman *et al.*, 2014a). Radioactive waste management practices relied on both the dilute–disperse and contain–confine strategies. Only for the latter were volume reduction techniques sometimes applied. Disposal practices included marine and land disposal either in the form of mounds, near surface or underground. These practices have been responsible for large contamination problems and exposing people to elevated radiation doses, which has led to the development of new disposal designs (Rutgers, 1996; IAEA, 2005a). Table 9.1 summarizes these practices; as listed in the table, only surface, near surface and underground disposal options are currently practised using new system designs (Abdel Rahman *et al.*, 2014b). New designs utilize the contain–confine strategy; they intend to isolate the wastes from the accessible environment during a period sufficiently long to allow substantial decay of the shorter lived radionuclides and, in the longer term, to limit release of the remaining long-lived radionuclides (Abdel Rahman *et al.*, 2005a, 2010). To achieve this aim, the multi-barrier concept that relies on engineered barriers to augment natural barriers has been developed. In this chapter lessons learned from old disposal practices will be reviewed with a special reference to the hydro-fracture grout practice. New disposal designs, performance assessment and safety case will be discussed in detail and different modelling approaches that could be used in conducting performance assessments will be introduced. Finally, the methods to assess the performance of cementitious materials in the disposal will be presented.

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Table 9.1 Historical disposal practices

Disposal option	Operation	Disposal sites	Disposed wastes
Marine	1946–1994	About 80 sites	Liquids diluted or unconditioned packages to sea bottom Solid were solidified in cement or bitumen and packaged in metal containers Unpackaged solids, including large parts of nuclear installations
Mounds	1945–	Worldwide	Unconditioned with no specific package requirement
Near surface	1945–	Worldwide	Unconditioned with no specific package requirement Currently the multi-barrier concept is applied
Deep well injection	1963–	Russian Federation	Liquid low-, intermediate- and high-level wastes unconditioned
Hydrofracture grouting	1964–1984	USA	Cement-waste grout injected under ground
Underground	1940–	Czech Republic, Hungary, Germany, Sweden, Finland, USA	Solid low- and intermediate-level wastes

9.1 Historical Disposal Practice

A variety of disposal options have been historically practised for low- and intermediate-level radioactive wastes, where high-level wastes and spent fuel disposals were postponed due to the realization of the difficulties in sustaining technical and economic resources over extended periods of time. Disposal practices were performed, at that time, under the control of national authorities in the absence of assessment approaches and regulations structure as known currently (Abdel Rahman *et al.*, 2014b). Lessons learned from these practices have led to great enhancement in the design of new disposal facilities.

Historically, land disposals have been experienced mainly as shallow excavated trenches similar to that of municipal solid wastes. These trenches were located in both humid and dry environments. The experience from operating such facilities in humid areas has contributed in improving the hydrological waste containment in new disposal designs. For instance, in the USA at the Maxey Flats site in Kentucky and the West Valley site in New York shallow disposal trenches were used to dispose of low-level radioactive wastes. Due to water infiltration into the trenches, bathtub effects were observed where the infiltrated water caused liquid waste containers to corrode leading to potential radionuclide releases. The trenches were hosted in a soil characterized by its coarse-grain deposits, which allowed the released radionuclides to migrate into the subsurface. Increased infiltrations were noticed in some trenches that experienced cap failure. These events were taken into account to improve land disposal practices, as discussed in Section 9.2. Also, worker behaviour during the operation led to accidental spillage of waste, direct disposal of contaminated liquids on the slopes of the site and spreading of liquid from the trenches by earth moving equipment (Rutgers, 1996).

Disposal practices such as hydro-fracture grout pumping have been carried out historically to stabilize and dispose of nuclear wastes for many years. Within this practice Oak Ridge National Laboratory, USA developed a process which involves pumping of a premixed grout of cementitious material and liquid wastes into beds of Conasauga shale underground. The pressure under which the grout is pumped acts to fracture the shale allowing the grout to penetrate along the horizontal bedding planes of the shale in layers. Low- and intermediate-level radioactive wastes composed of a mixture of all kinds of generated liquid wastes including those produced from hot-cell, pilot-plant and reactor operations besides volume of organic reagents and solvents were stabilized and disposed of using this technique. The waste streams were treated using evaporation for aqueous streams, the resultant wastes from evaporator were reported to contain up to 2 Ci of beta–gamma activity per gallon. ^{137}Cs was the major radionuclide, while ^{90}Sr was presented at a level of only 0.1 Ci/gal. or less. The major alpha activity was found for ^{244}Cm with a maximum concentration of about 1 mCi/gal. (Stinton *et al.*, 1983). Within this technique, the radioactive wastes were poured and pumped to tanks from where the wastes were mixed with predetermined weights of dry cement, fly ash, clay minerals and delta gluconolactane which retard setting time (Fuhrmann *et al.*, 1981).

Four experimental and industrial injection wells were installed at the Oak Ridge site. To study the performance of the practice before applying it, experimental injection wells (HF-1 and HF-2) were constructed. Twenty-four observation and monitoring wells were installed surrounding the injection well. The cement grout doped with radioactive tracer was injected into the Pumpkin Valley Shale. The performance of the grout was found acceptable and industrial injection wells (called old and new hydrofracture facilities) were constructed (Whiteside *et al.*, 2002). The old hydrofracture facility started to operate in 1964 and ceased operation in 1980 whilst the new hydrofracture facility operated from 1980 to 1984. The old facility consisted of an injection well, five underground liquid low-level radioactive waste tanks, a waste pit and a pond to support disposition of low-level waste. More than 2 million gal. of waste streams have been injected containing a total activity of 600 000 Ci ($1\,\mathrm{Ci} = 3.7 \times 10^{10}\,\mathrm{Bq}$) during the period 1966–1978 (Reed, 1984). The total disposed activities reached 1.5 million Ci; the principal nuclides are ^{90}Sr and ^{137}Cs although others, including ^{3}H, ^{60}Co, ^{106}Ru and isotopes of U, Am and Pu existed (Stow *et al.*, 1985). By the end of the operation the estimated injected waste volume had risen to 3.2 million gal. After the facility shutdown, the five tanks contained 199 220 L of wastes (LaForest *et al.*, 2001).

The stabilized radioactive wastes that resulted from the operation of the old hydrofracture facility form a grout sheet at 800–1000 ft below ground which is estimated to be up to 1600–3200 ft wide and 0.25 in. thick. The new hydrofracture facility produced a stabilized grout sheet about 1000–1100 ft underground which is estimated to be 4000 ft in diameter (Gault, 2007).

A recent hazard assessment document concluded that no credible accident scenario could release the stabilized material inventory due to the physical properties of the grout and the lack of credible energy resource that could impact the material at 800–1100 ft under soil, rock and shale (Department of Energy, 2008).

The remediation of the site included many actions, among them the plugging and abandoning of 100 associated monitoring wells and boreholes was performed. Decontamination and decommissioning of the old hydrofracture facility structures and equipments were planned to be completed before installation of a cap on the solid waste storage area. The new hydrofracture facility remediation action included demolition of the above-grade structures (e.g. Building 7860, bulk storage bins) whilst the below-grade structure and equipment (e.g., piping, valves, pumps) were planned to be grouted in place. The contents of underground tanks T-13 are planned to be removed, and the tanks' shell will be grouted in place (Oak Ridge Reservation, 2002).

9.2 Disposal Facility Design

The disposal facility is a passive safety system designed to provide adequate isolation of the waste over disposal lifetime without any human interference. This means that any releases from the facility must be below health-based limits at any time in the future. To achieve this goal, a multi-barrier concept was recently developed and implemented. This concept enables the designer to rely on the overall disposal system to ensure safe performance rather than focusing on a single part of the system. The designer has to optimize the components of both the natural and engineered barrier systems to isolate and retard radionuclide migration into the surrounding environment and to dilute the effect of the released radionuclides on the biosphere (Abdel Rahman *et al.*, 2014a). The optimization of the natural barrier is performed during site selection.

Disposal options are categorized based on the depth of the facility location as either geological or near surface. Near-surface disposal includes two types of disposal systems, namely shallow facilities and rock cavities or abandoned shallow mines. Historically, shallow disposal units were located either above the land surface in the form of mounds or below the ground surface as trenches, borehole, vaults, pits, and so on. Nowadays, new shallow land disposal design is restricted to near-surface facilities. On the other hand, geological disposal for high-level wastes and spent nuclear fuel have been studied extensively. Various underground laboratories have been established and are carrying out integrated programmes to assess the performance of different host geological media. These programmes comprise various experiments to study and model contaminant migration, water and heat transport and geo-mechanical tests; in addition, intensive modelling efforts were also initiated to study long-term performance of the geological subsystem in each host media such as the saturated and vadose zone (Abdel Rahman, 2012).

Each of these options utilize engineered barriers similar to those used in municipal landfills such as liner, drain and cover. Other engineering barriers are used in radioactive waste disposal to prevent and/r minimize the radiological hazard associated with possible releases of these wastes. These barriers include wasteform, package, backfill and structural walls. Each of these barriers has one or more specified functions. Table 9.2 lists the different barriers, their function and the materials utilized (IAEA, 2001a, b). The requirements for the

Table 9.2 *Engineering barriers in radioactive waste disposal*

Barrier	Function	Material
Waste form	Mechanical strength	Hydraulic binder, for example cement
	Limit water ingress	Polymer, bitumen
	Retain radionuclides	Glass-ceramic
Package	Shield	Concrete
	Mechanical strength	Steel
	Limit water ingression	
	Retain radionuclides	
Backfill	Void filling	Cement based
	Limit water infiltration	Clay based
	Radionuclide sorption	
	Gas control	
Buffer material	Protect the waste against external tectonic impacts	Clay based
	Protect against chemical attack of dissolved elements and microbes	
Structural materials	Physical stability containment barrier	Concrete Steel
Liner	Limit water infitration	Clay
	Retain mechanical stability under compressive and shear strength	Geopolymer
Cut-off walls	Limit horizontal groundwater migration into the facility	Concrete
	Provide structural integrity during operational phase	Cement-clay
	Assess radionuclide sorption	
Cap	Limit water infiltration	Clay
	Control of gas release	Gravel/cobble
	Erosion barrier	Geotextile
	Intrusion barrier	
Drains	Control leachate	Gravel-sand
	Enable monitoring	

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wasteform were derived based on lessons learned from historical disposal that include but are not limited to (Rutgers, 1996):

- Waste must be immobilized with low leaching rate of radionuclides to avoid container corrosion and retain radionuclide.
- Waste should have acceptable mechanical behaviour to avoid slump cap.

The lifetime service of any disposal practice is mainly determined based on the half-life of the major disposed radionuclides. For low- and intermediate-level wastes with short-lived radionuclides, the service time is in the range of a few hundred years depending on the national regulation. This leads to increased caution during the design process to assess both current and anticipated barrier performance. For example, the package, which after the wasteform is the second engineering barrier in the multi-barrier concept, is designed to meet intensive regulatory requirements to ensure its shielding, containment and mechanical performance. For low- and intermediate-level wastes, some regulations require meeting specifications on the thickness, homogeneity, compressive and traction strengths, resistance to radiation and thermal cycling (Ouzounian and Poisson, 2011). For high-level wastes and spent fuel, the vitrified wastes are inside a special package (canister). Stainless steel or iron containers were proposed for high-level wastes; this package is designed to provide isolation for 1000 years (Pusch, 2008). Spent fuel canisters are made of copper and iron/steel and prototypes manufactured and tested.

Disposal design starts during the project planning phase and continues through its life cycle. The design process is divided into conceptual, basic and detailed design. The main objective of the conceptual design phase is to select a suitable disposal option; the decision on the suitability of the option is usually based on initial performance assessment. Input data for such assessment are estimated radioactive waste inventory and characteristics and generic site characteristics (IAEA, 1992; Abdel Rahman, 2011). At the basic design phase, the designer has to confirm that the selected disposal option could become a licensable operational option. During this stage, the design is expanded; site specific information is incorporated; technical feasibility of materials is carried out; and the data gaps are identified. Finally in the detailed design phase, a detailed performance assessment is conducted that is used to acquire a construction licence.

The multistage iterative nature of the design process allows the designer to modify the design to achieve optimum performance that meets regulatory requirements and is consistent with good engineering practice, operational needs and cost constraints. To evaluate the disposal performance, information of the wasteform, engineering barrier materials and site characteristics are required. The quality of the required information is largely dependent on the design phase (Abdel Rahman, 2011). The details of the performance assessment process will be presented in Section 9.4; the rest of this section is devoted to present various disposal options.

9.2.1 Shallow Land Disposal Options

Covered trench. This is the oldest and simplest disposal concept; the site could contain more than one module, each module is an excavated trench and the cover is a single low-permeable cap. The disposal site at Vaalputs in South Africa is an example of this concept. In 1978, a programme was launched to select a suitable site for the disposal of nuclear waste in South Africa. Detailed studies showed that a locality some 100 km south east of Springbok (600 km north of Cape Town) was ideally suited for the disposal of low- and intermediate-level wastes. The initial stage of investigations culminated in 1983 when three farms, which now constitute the Vaalputs Radioactive Waste Disposal Facility, were acquired by the State on behalf of the Nuclear Energy Corporation of South Africa (Necsa), which is responsible for its management. The first low- and intermediate-level wastes were delivered in October 1986 (Figure 9.1).

Mound. This design is based on disposing of the wastes above the ground. The La Manche disposal facility in France is an example of such a facility. This site was authorized at 1969 and continued to work till 1994. For that site, the trench option was applied for a year and due to the high precipitation rate and ground stability problems, a decision was taken to

Figure 9.1 *Disposal of low and intermediate level radioactive wastes at Vaalputs, South Africa. Reproduced with permission from M. Ojovan*

adopt the mound concept. The soil was levelled, isolated using bitumen, and a concrete framework structure was built to accommodate the wastes. After detection of tritium leakage, the waste was retrieved and new engineering barriers were installed including package, concrete platform, drainage system and multilayer cover (Chino *et al.*, 1999). Figure 9.2 shows a schematic diagram of the La Manche disposal structure and a photograph of the facility after closure (Potier and Gallagher, 1998). As shown in this figure, the disposal facility accommodates monoliths and tumuli structure. Monoliths are units with reinforced concrete walls based on top and bottom slabs that were constructed below the ground level. The unit capacity varies from 50 to 80 m^3 and hosts intermediate- and low-level waste packages. On the other hand, tumuli are constructed above the ground over the monoliths. It accommodates very-low-level waste in concrete containers and metallic drums and is backfilled with gravel (Potier and Gallagher, 1998).

Closed vault. This consists of a concrete vault into which the waste packages are placed. The void may be backfilled and the structure closed with concrete slabs, which may be sealed by asphalt. The whole structure is then protected by an earthen cap. Examples of the application of this concept are in Centre de l'Aube in France, El Cabril in Spain and Rokkasho-mura in Japan. El Cabril starte doperation in 2008; the disposal of low- and intermediate-level wastes will take place in two platforms that are planned to accommodate 28 disposal cells (ENRESA, 2013a, b). Work at the Centre de l'Aube disposal site started in 1984 and operation began in 1992. The disposal site hosts 420 disposal vaults with a planned capacity of 1 000 000 m^3. The vaults are covered by movable steel-framed shelters to prevent rain water infiltration into the facility during operation (Figure 9.3). A drainage system is installed beneath the vaults to collect any infiltrated water for monitoring purposes. The facilities receive long-lived radioactive wastes in concrete containers and short-lived radioactive wastes in steel drums and the vaults are backfilled with gravel. In the closure phase, the vaults will be covered by concrete slab and lined with a waterproof coating (Potier and Gallagher, 1998).

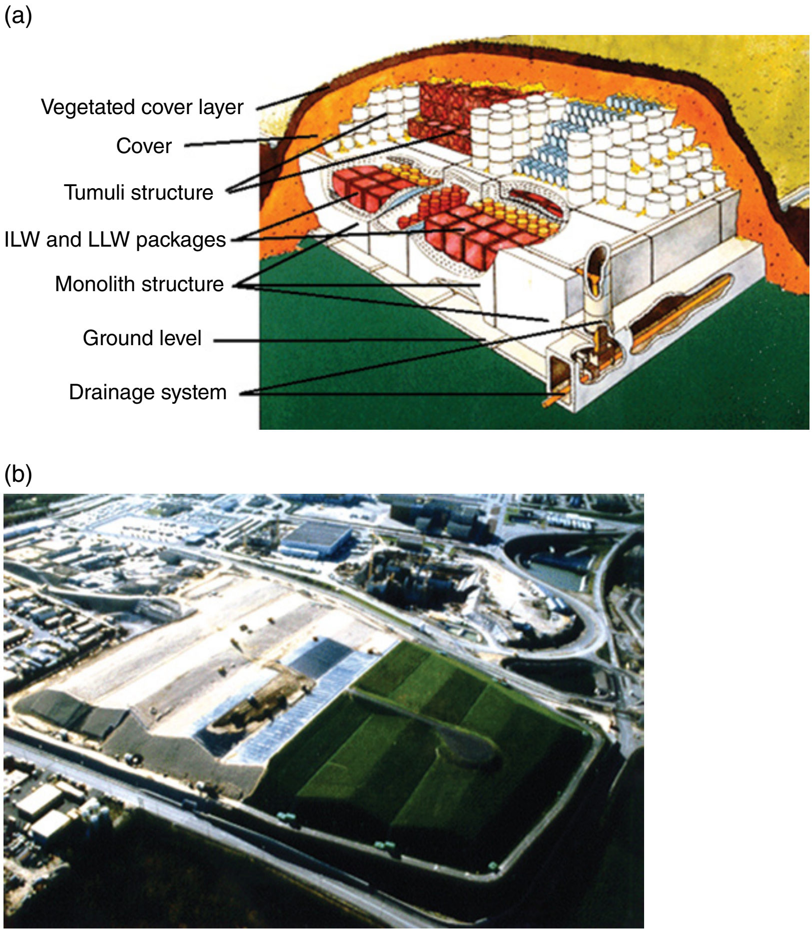

Figure 9.2 *(a) Schematic of the La Manche disposal structure. ILW, intermediate-level waste; LLW, low-level waste. Reproduced with permission from J.-M. Potier. © 1998. (b) Photograph of the La Manche disposal facility after closure (Potier and Gallagher, 1998). Reproduced with permission from J.-M. Potier. © 1998*

9.2.2 Underground Disposal Option

Various underground disposal options exist, most of them based on using old mines and cavities to accommodate the immobilized wastes.

Borehole (well disposal). This concept includes the emplacement of immobilized waste in a narrow diameter engineered borehole facility operated directly from the surface. Borehole disposal facilities cover a range of design concepts with varying depths and diameters (Abdel Rahman *et al.*, 2015). It was developed to dispose of disused radioactive sealed sources and low- and intermediate-level wastes that exceed the waste acceptance criteria for shallow facilities. This option was widely used in the Russian Federation and USA. In the Russian Federation, the facility is at a depth of 6 m whereas in the USA the borehole depth

Figure 9.3 Steel movable shelter for Centre de l'Aube (Potier and Gallagher, 1998). Reproduced with permission from J.-M. Potier. © 1998

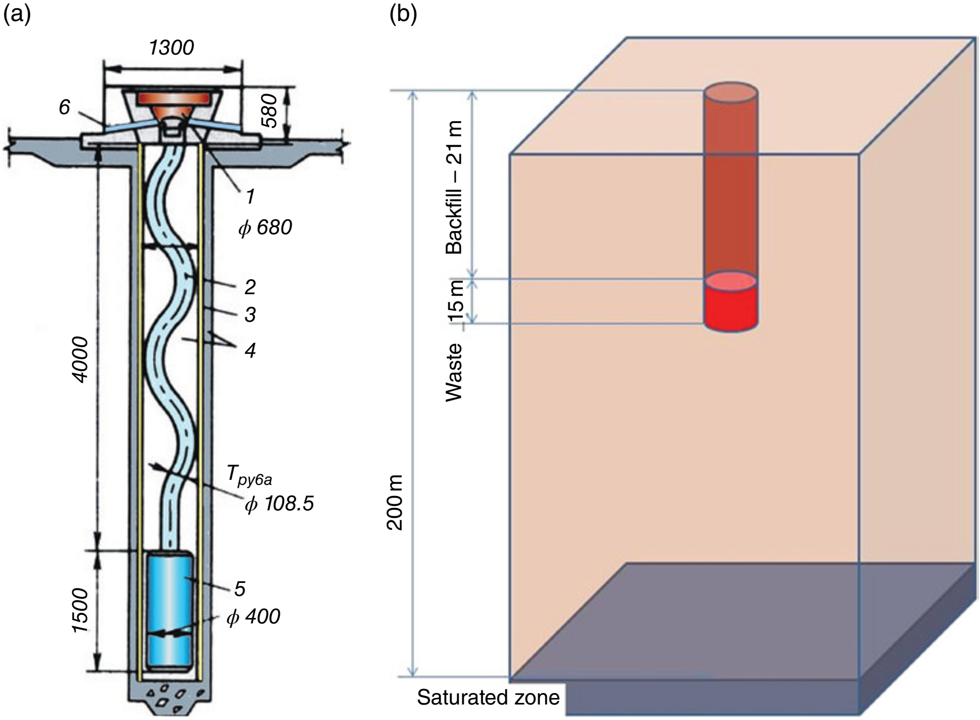

Figure 9.4 Borehole designed in (a) the Russian Federation and (b) the USA

is 36 m (IAEA, 2005b). In some current disposal borehole designs, the boreholes are lined, for example with reinforced concrete and stainless steel, and are filled *in situ* with cement grout or a low melting point metal alloy (IAEA, 2002). Figure 9.4 illustrates the borehole design used in the Russian Federeation and the USA.

Rock cavity and old mine. Both natural and excavated rock cavities were used to dispose of low- and intermediate-level wastes in different countries. Crystalline bedrock was selected to host the Finnish Olkiluoto and Loviisa disposal facilities which are located below groundwater table at depths greater than 60 m. Other disposal facilities were located in the vadose zone such as the Czech disposal facility Richard which is located in an abandoned limestone mine at a depth of 70–80 m. Rock salt was also selected to host radioactive wastes in Germany (ASSE and Morsleben).

9.3 Modelling Approaches

During the disposal project life cycle, many decisions have to be taken that include site selection, engineering design and waste amount and types. Once a site is identified and an initial engineering design is defined, a more detailed assessment of the disposal impact on the environment and human health under current and anticipated conditions is required to obtain legal and/or regulatory approvals for construction, operation and closure. A detailed safety assessment and/or presentation of a safety case in the form of a structured set of documents are required for granting these approvals (Abdel Rahman *et al.*, 2005b). Modelling is a phase in the integrated safety assessment of any disposal facility and, as illustrated in Figure 9.5, is considered as the core of this methodology as it is used to predict the behaviour of both engineering and natural barriers in the disposal and their impact on the surrounding environment over large time scales. Therefore building confidence in the modelling is a very important issue to ensure the defensibility and transparency of the safety assessment and/or safety case.

Modelling is a multi-step phase (Figure 9.6); the first step is the selection and justification of appropriate mathematical models that can best describe the conceptual models of the

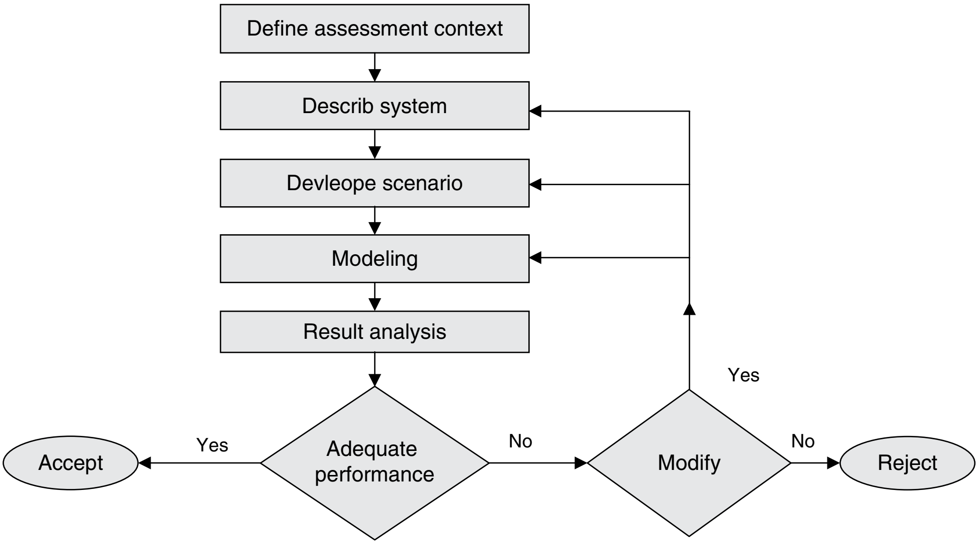

Figure 9.5 Integrated safety assessment methodology

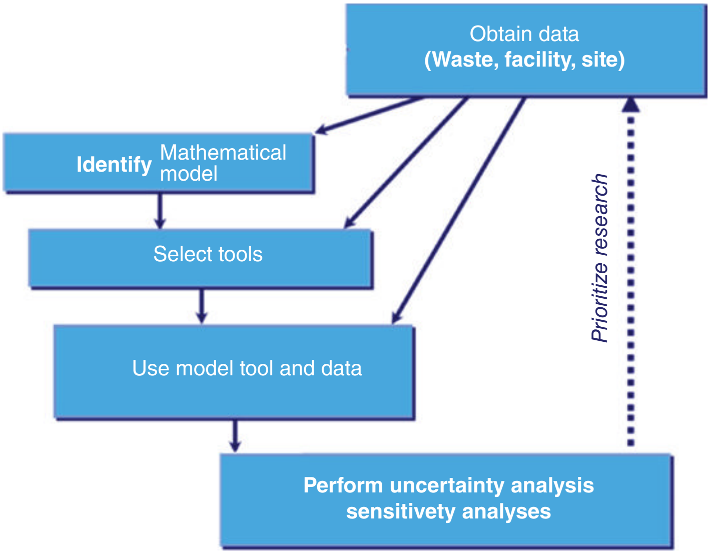

Figure 9.6 *Multi-step modelling phase*

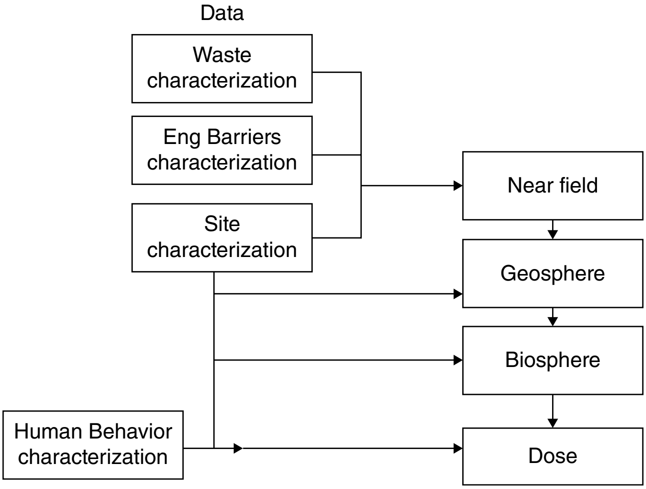

Figure 9.7 *Disposal components and their corresponding data*

system that resulted from the scenario development phase. The outputs of this step are sets of algebraic and differential equations with appropriate and adequate boundary and initial conditions that then need to be solved. Usually modelling is performed by schematically dividing the disposal system into its main components; Figure 9.7 illustrates these components and the type of data required for each component (IAEA, 2004). There are two modelling approaches that could be adopted in assessing the disposal safety, namely deterministic and probabilistic. The deterministic approach relies on simulating the system behaviour using a single value for each parameter whereas in the probabilistic approach the parameter

Table 9.3 Deterministic and probabilistic modelling approaches (NUREG, 2000)

Point of comparison	Deterministic	Probabilistic
Outcome	Single estimate of performance	Distribution of potential outcomes
	Conservative estimation	Realistic estimation
Features	Relying on bounding analysis of uncertain parameters	Parameter uncertainty is performed to attain defensible distribution
	Bound models	Model uncertainty is performed
	Use simple model assumptions, and parameters that can be demonstrated as conservative	Used for complex systems with large number of parameters
	Does not provide insight into the quantitative margin of safety within bounding analysis	Provide insights into the quantitative margin of the analysis

is defined with a statistical distribution (IAEA, 2003). The selection of any of them is affected by the regulatory requirements, data availability and stage of the project. A comparison between these two approaches is shown in Table 9.3 (NUREG, 2000). Examples of source term models and dose assessment modelling approaches used in different disposal projects are presented in Table 9.4 and Table 9.5 (PAMINA, 2011; Drace *et al.*, 2012).

Tool selection and justification is the second step in the modelling phase, at which empirical, analytical or numerical solution of the conceptual model is acquired. It might be acceptable to develop a mathematical model to be consistent with the immediately available tools due to limited resources. When this approach is taken, the reasons for adopting the approach should be explained and the associated limitations documented (IAEA, 2004).

The third step in modelling is acquiring defensible data, data usually divided into disposal system parameters, human exposure parameters and radionuclides/element parameters (IAEA, 2004). It should be noted that the quality of the data is dependent on the assessment phase and the stage of disposal development. Figure 9.8 shows the relationship between radioactive waste design phases and the quality of the data (Abdel Rahman, 2011).

During this step it is important to document the treatment of uncertainty associated with the temporal and spatial variability of these parameters. It is worth noting,that the justification of the quality of data is interrelated with the disposal stage. The final step in the modelling phase is running the model and presenting the results.

9.4 Performance Assessment

Performance assessment is the quantitative analysis of some subset of processes relevant to the behaviour of the disposal system and calculation of intermediate parameters of interest followed by a comparison of intermediate parameters with appropriate criteria set by regulation design targets. The hierarchy of the radioactive waste disposal assessment terms is shown in Table 9.6 (Miller *et al.*, 2000). The assessment context is the first phase at which purpose, regulatory framework, assessment end-points, assessment philosophy, disposal

Table 9.4 *Assessment models for different disposal components. Failure and release source term models*

FEP	Model type	Parameter	Model equation	Data required	Tool
Carbonation	Empirical	Carbonation penetration depth, *X*	$X = \left(2D_{\text{ef}} \dfrac{C_{\text{gw}}}{C_s} t \right)^{0.5}$	D_{ef}, Ca diffusion coefficient in concrete C_s, Portlandite bulk concentration in concrete C_{gw}, total inorganic carbon concentration in groundwater or soil moisture t, elapsed time	Excel
Sulphate attack	Empirical	Deterioration depth, *x*	$x = 1.86 \times 10^6 C_s \left(C_{\text{Mg}} + C_{so_4} \right) D_i t$	C_s, wt% aluminate in cement C_{Mg}, Mg^{2+} concentration in solution C_{SO4} , sulphate concentration in solution t, time D_i, intrinsic diffusion coefficient in cement	Excel
	Mechanistic	Degradation rate, *R*	$m = m_c \log\left(\dfrac{t_{\text{spall}} C_\circ}{t_r C_k} \right) \quad \int \quad m \prec m_c$ $m = m_c \qquad m \succ m_c$ $C_{\text{E}} = m \left(\dfrac{\text{mass}}{\text{volume}} \dfrac{\text{cement}}{\text{concrete}} \right)$ $X_{\text{spall}} = \dfrac{2\alpha\gamma(1-v)}{E\left(BC_E\right)^2}$ $t_{\text{spall}} = \dfrac{X^2 C_E}{2D_i C_\circ}$ $R = \dfrac{EB^2 C_E C_\circ D_i}{\alpha\gamma(1-v)}$	C_k, sulphate concentration at time k C_o, sulphate concentration in solution C_{E}, concentration of reacted sulphate, ettringite E, Young's modulus m, reacted sulphate quantity m_c, value of m at the end of reaction t_{spall}, characteristic time for reaction α, roughness factor for fracture pain B, linear strain caused by 1 mol of sulphate reducing in 1 m^3 γ, fracture energy of concrete v, Poisson's ratio	

(*continued*)

Table 9.4 (*continued*)

FEP	Model type	Parameter	Model equation	Data required	Tool
Leaching of radionuclide	Mechanistic	CLF	$\mathrm{CLF} = Q_o[1 - \exp(-kt)]$	k, reaction rate constant Q_o, fraction of radionuclides on surface	Excel
			$\mathrm{CLF} = 2\left(\frac{S}{V}\right)\sqrt{\frac{Dt}{\pi}}$	D, effective diffusion coefficient	
			$\mathrm{CLF} = \left(\frac{S}{V}\right)U_o t$	U_o, network dissolution rate	
Coupled flow and transport though unsaturated barrier			$\xi \frac{\partial \psi}{\partial t} = \frac{\partial}{\partial x}\left[k(\psi)\frac{\partial \psi}{\partial x}\right] + \frac{\partial}{\partial z}\left[k(\psi)\frac{\partial \psi}{\partial z}\right] -$ $\frac{\partial}{\partial z}k(\psi) + W$		
			$\frac{\partial \theta RC}{\partial t} =$ $\frac{\partial}{\partial x}\left[\theta\left(D_{xx}\frac{\partial C}{\partial x} + D_{xz}\frac{\partial C}{\partial z} - CV_x\right)\right]$ $+\frac{\partial}{\partial z}\left[\theta\left(D_{xzx}\frac{\partial C}{\partial x} + D_{zz}\frac{\partial C}{\partial z} - CV_z\right)\right]$ $+I$	ξ, soil moisture capacity, $\xi = \delta\theta/\delta\psi$ θ, volumetric water content ψ, water head pressure k, hydraulic conductivity W, source/sink term R, retardation coefficient C, contaminant concentration I, source/sink term	Numerical tool GoldSim
Saturated barrier			$\frac{\partial C_w}{\partial t} = \frac{D_w}{R_d}\left[\frac{\partial^2 C_w}{\partial x^2} + \frac{\partial^2 C_w}{\partial y^2}\right] - \lambda C_w$ $R_d = (1 + K_d \rho_d/\varepsilon)$	C_w, concentration (Bq/ml) D_w, diffusivity (cm^2/s) λ, decay constant R_d, retardation coefficient ε, effective porosity of barrier ρ_d, barrier bulk density (g/cm^3) K_d, contaminant distribution coefficient (cm^3/g)	Numerical tool GoldSim

CLF, cumulative leached fraction.

Table 9.5 Dose assessment models in some disposal projects

Disposal	Assessment model	Tool
NRI-RAWA (Czech Rep.)	Algebraic expression	Excel, AMBER, GoldSim V9.6
Posiva (Finland)	Biosphere assessment database	BSAdb
	Biosphere models based on MATLAB/Simulink	PANDORA/EIKOS
Andra (France)	Integrated modelling package for safety assessment	Aquabios/MoM
GRS-B (Germany)	Integrated modelling package for safety assessment	EMOS/EXCON/EXMAS
Enresa (Spain)	Assessment model	AMBER

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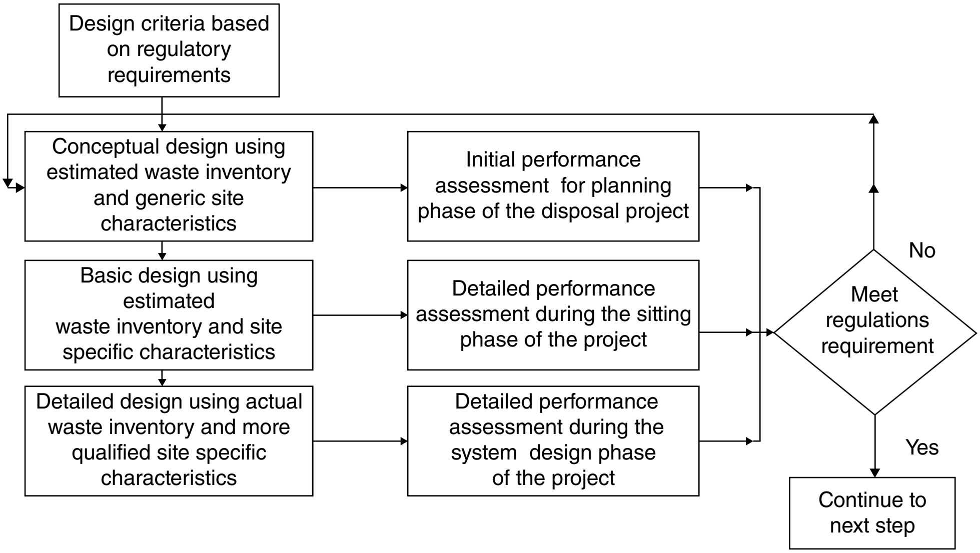

Figure 9.8 Relationship between different low-level radioactive waste disposal design phases and quality of information

system characteristics, and timeframes are identified based on the stage of the project. Then the system is divided into its main components, that is source term, near field and far field.

For each component Features, Events and Processes (FEPs) that affect radionuclide release and the decision to include or exclude these FEPs is either based on regulatory guidance or taken because these FEPs have a positive effect on the release (i.e. retain or retard the contaminants). Based on the selected FEPs, release scenarios are developed which handle future uncertainties directly by describing alternative futures and allow for a mixture of quantitative and qualitative judgements. This is achieved by investigating the importance of uncertainty sources based on exploring release trends under varying conditions. Release scenarios are translated into a conceptual model that describes with words and diagrams the key processes that occur within the studied component (or have a reasonable likelihood of occurring).

Table 9.6 *Hierarchy of commonly used terms relating to the assessment of radioactive waste disposal*

Safety case	
Includes performance and safety assessments. In addition, a full line of arguments and evidence that a sufficient set of processes have been analysed and appropriate models and data used; relevant overall measures of performance and safety are within acceptable ranges, allowing for uncertainties. More qualitative, parallel lines of evidence and reasoning may be also used to support results of the quantitative modelling and to indicate the overall safety of the system	
Performance assessment Includes performance analysis. In addition, comparison of intermediate parameters with appropriate criteria set by regulation design targets	Safety assessment Includes safety analysis. In addition, testing of arguments that a sufficient subset or processes have been analysed, appropriate models and data used, plus comparison of calculated measures of overall performance to regulatory safety limits and targets
Performance analysis Quantitative analysis of some subset of processes relevant to the behaviour of the disposal system and calculation of intermediate parameters of interest	Safety analysis Quantitative analysis of the set of processes that have been identified as most relevant to the overall performance of the disposal system and calculation of a measure of overall performance relevant within the given national regulatory regime

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During the development of the conceptual model the geometry and dimensionality of the studied module, initial and boundary conditions, time dependence and the relevant physical and chemical processes of the developed scenario are defined (IAEA, 2004; Abdel Rahman and Zaki 2011). There are different methods to develop the conceptual model, one of them is depending on the expert judgement and the experience of the assessment team (SACO approach). The interaction matrix approach is another method that could be used to develop the conceptual model; it relies on the graphical representation of system interactions through the use of formalized procedures and expert judgement. A full description of these methods is discussed elsewhere (IAEA, 2004). The developed conceptual model forms the basis for the selection of mathematical models, which in turn govern the selection and creation of numerical models and computer codes (Abdel Rahman *et al.*, 2009).

9.5 Safety Case

To support the decision making process throughout the disposal lifetime, the safety case concept is developed. Currently, it is at the top of the hierarchy of the assessment terms that are used in disposal projects, as indicated in Table 9.6. Safety case is the combination of safety and performance assessments of the repository linked with other factors that are important for the assurance of safety such as the use of sound science and engineering, Quality Assurance procedures, safety culture, robustness and defence in depth, and institutional controls (Miller *et al.*, 2000).

The use of safety case enables interested parties to participate in the decision making process by communicating their level of confidence in the project at a given stage. The main elements that contribute to the safety case are safety strategy, assessment basis, evidence and arguments for safety and a synthesis statement. Safety strategy is the adopted approach to achieve safe disposal, it aims to incorporate good management and engineering principles and practice. The main elements in the safety strategy include the overall management strategy, sitting and design strategy and assessment strategy. The adaptation of good management strategy can provide sufficient information and flexibility to use advances in scientific understanding and engineering techniques. Sitting strategies tend to minimize uncertainty through the selection of a geological setting with assessable features. The assessment strategy must ensure that the safety assessments detect and analyse relevant conditions and processes.

The assessment basis is the collection of information and analysis tools supporting the safety assessment. This includes an overall description of the disposal system that consists of the chosen repository and its geological setting; the scientific and technical data and understanding the relevance assessment of a system safety; and the assessment methods, models, computer codes and databases for analysing system performance. The quality and reliability of a safety assessment depends on the quality and reliability of the assessment basis. Assessment results must be analysed by comparison against specified safety criteria, the evaluation of the performance measure should be accompanied by more qualitative arguments that provide a context or support for the performance-calculation results. The safety case robustness may be strengthened by the use of multiple lines of evidence, leading to complementary safety arguments, to compensate for any shortcomings in confidence in any single argument (OECD, 2007).

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10

Future Trends and Concluding Remarks

10.1 Role of Cementitious Materials

Cementitious materials are crucial for contemporary industries. Portland cement for example is one of the most widely consumed construction products. Its world production is about 3 billion t per year. In some countries, cement is 10% of the gross domestic product and cement production employs 8% of the global workforce. The nuclear industry is no exception and uses the advantages offered by cements. In nuclear waste management cements are attractive because they have favourable physical and chemical properties to host radioactive and hazardous nuclides and to act as an effective barrier to their release and migration. Physically cement is a durable solid material with a low permeability in its hardened state which protects the radioactive waste, facilitating its safe transportation and storage. Chemically cement pore water has a high pH and the constituent products of cement favour sorption and substitution of cationic, anionic and neutral radioactive waste species into cement solids while the microstructure affords physical immobilization. Cement is inexpensive and a readily available material, durable in its hardened state but fluid when initially cast, compatible with a variety of wastes both in solid and liquid states. Cements have been extensively modified by reactive admixtures to enhance physical properties and tailor the immobilization potential for specific waste species or groups of species and counter the potentially harmful effect of inactive waste species.

Cements are the main construction materials in nuclear facilities including storage and disposal facilities. Cementitious materials are essential for radioactive waste disposal. The disposal is a passive system that utilizes the multi-barrier concept to ensure the protection of human health and the environment from the radiation hazards. Regulatory requirements for the safe disposal practice include provisions on the containment performance; these provisions

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Ravil Z. Rakhimov, Nailia R. Rakhimova and Michael I. Ojovan.

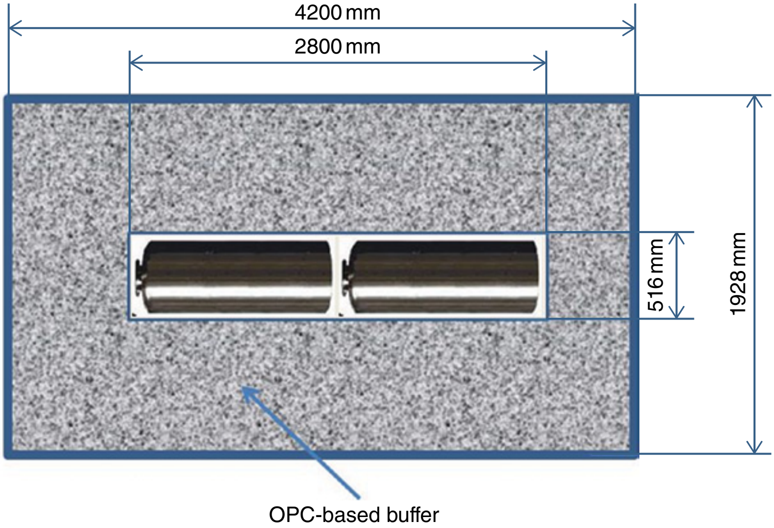

Figure 10.1 *Schematic of supercontainer design. OPC, ordinary Portland cement*

imply the assessment of the disposal performance over 300 years for short-lived low-level radionuclides and for thousands to hundreds of thousands of years for long-lived low-, intermediate- and high-level radioactive wastes. Cements are also the main materials for low- and intermediate-level waste immobilization (Glasser, 2011). They are currently proposed as an important component for the disposal of high-level radioactive waste in a so-called supercontainer concept (Bel *et al.*, 2006).

The cylindrical supercontainer comprises a carbon steel overpack surrounded by an ordinary Portland cement shell (OPC-based buffer) and a stainless steel liner (Figure 10.1). The OPC-based buffer has been chosen to provide a highly alkaline chemical environment which will last for many thousands of years so that the external surface of the overpack remains passivated and the overpack corrosion is inhibited. The concrete buffer also has low-hydraulic conductivity to slow the infiltration of external fluids to the overpack surface, and provides radiological shielding.

10.2 Novel Cementitious Materials

Cementation processes are now regarded as technically mature and proven waste conditioning technologies although novel approaches are continuing to be devised. Most of the existing technologies have been developed for conditioning of large amounts of operational radioactive waste from nuclear power plants and other nuclear fuel cycle facilities. New waste streams including legacy and decommissioning activities required improved material performance and technologies. Selection of waste conditioning technologies and suitable cements is typically specific to the waste streams involved. The nuclear industry generates a wide variety of potentially soluble and therefore highly mobile wastes which require immobilization. The wastes differ from country to country, depending on the size and scope of the nuclear programme. For example, fuel reprocessing tends to generate chemical wastes containing

Table 10.1 *Representative novel cementitious materials*

Designation	Formation conditions	Comments
Calcium sulphoaluminate cement (CSAC or C\$AC, where \$ = SO_3)	Available commercially or made by mixing commercial CAC with calcium sulphate	This has a history of use (~40 years) as a construction cement. Developed in China but now widely available
CAC	Based on clinkers or fused products with dicalcium silicate and $CaAl_2O_4$	CACs are widely available as commercial products with a long history of use in construction
Geopolymer SIAL	Mixture of sodium silicate (hydrate) with metakaolin	Geopolymer-type matrix which is characteristically X-ray amorphous
Magnesium phosphate cement	Mixture of fine grained MgO (periclase) and a phosphate source (e.g. phosphoric acid or monopotassium phosphate)	Many variants are known, differing in pH and solubility. Not fully commercial except for small-scale applications (e.g. as refractory or dental cements)

tributyl phosphate ($PO(OC_4H_9)_3$) and salt enriched wastes whereas pond storage of spent nuclear fuel tends to generate mainly spent ion exchangers, organic and inorganic. Most of these wastes can be successfully immobilized directly into Portland cement although often only at low loadings. In some cases, volume reduction is improved by chemical pretreatment of wastes or by using blended cements containing mixtures of fly ash, slag or silica fume with Portland cement. In other cases selected sorbents such as zeolites or bentonite clay can be incorporated into the formulation. Moreover limitations in the properties of Portland cement have led to the development of novel binders. An example is the stabilization of soluble zinc salts: they interfere with hydration of Portland cement but are well tolerated in calcium sulphoaluminate cements (CSACs, see Section 4.2). Some novel cementitious materials have a history of commercial use and are known to be durable in a range of natural service environments. Standards are also available for CSACs and calcium aluminate cements (CACs, see Section 4.1). The International Atomic Energy Agency (IAEA) has evaluated four types of novel cementitious materials as summarized in Table 10.1 (IAEA, 2013).

It has been noted that the most engineering experience has been achieved with CAC and CSAC. It has also been noted that the geopolymer type materials [e.g. SIAL made from alkali silicate (Na, K) and metakaolin] are both new and old. They are old in the sense that they have a history of patenting and small-scale application extending over more than a century but novel inasmuch as they have only recently been considered for use in structural and large-scale applications. The favourable experiences suggest that more widespread applications to waste conditioning are possible. The SIAL geopolymers have demonstrated leachability indexes (LIs) (see Equation 8.9) above 11 which significantly exceed the required threshold LI = 6. The Slovak Nuclear Authority have granted permission to use geopolymers for safe disposal of radioactive waste since 2003 (IAEA, 2013). Various remotely operated devices have been used for radioactive sludge and resins solidification at the A-1 and V-2 nuclear power plants (NPPs) in Jaslovske Bohunice (Slovak Republic), at the Mochovce NPP (Slovak Republic), and at the Dukovany and Temelin NPPs (Czech Republic). Utilization of geopolymers in

Figure 10.2 *(a) Egyptian pyramids. Reproduced with permission from P. Yakovlev. According to Davidovits' theory, they have been cast on site and are composed of blocks made of geopolymers. (b) Concrete containers. The long-term durability of cementitious materials is crucial to ensure safe immobilization of nuclear waste. Reproduced with permission from M. Ojovan*

nuclear waste immobilization is a perspective option despite the lack of standards for the precursors and experience of process optimization. The long-term stability of geopolymeric materials is also a scientific problem. The binding phase of geopolymers is an amorphous rigid alkali aluminosilicate gel similar to glasses about which little is known. Research activity in the area of geopolymers is high and is likely to generate more knowledge including on their long term durability which will contribute to confidence in the application potential of geopolymers in the nuclear field. It should be noted that discussions are under way on real history of utilization of geopolymers compared with conventional cements (Figure 10.2). Davidovits examined building blocks of some of the major pyramids and concluded that, rather than being blocks of solid limestone hauled into position, they are composed of geopolymers, cast in their final positions in the structure (Davidovits, 2013). According to his theory, a soft limestone with a high kaolinite content was quarried in the *wadi* on the south of the Giza plateau, then dissolved in large Nile-fed pools to became a watery slurry. Lime and natron used by the Egyptians in mummification was mixed in and the pools were then left to evaporate, leaving behind a moist, clay-like mixture. This grout-type mass would be carried to the construction site where it would be packed into reusable wooden molds and over the next few days the mixture would undergo a chemical hydration reaction similar to the setting of cement.

The durability of cementitious materials is an extremely important issue within nuclear waste management. Testing and the extrapolation of short-term test data to centuries (or longer) has proved to be very complex therefore natural and historical analogues play a significant role in performance assessment of materials (Alexander, 1995; Miller *et al.*, 2000). Although it is generally accepted that cementitious materials can be engineered to perform over long times (based on analogy with natural, archaeological analogues and old structures), methods for quantifying such long-term service are not standardized (Bart *et al.*, 2012).

10.3 Concluding Remarks

Cementitious materials are essential parts in any radioactive waste facility. This book provides the reader with both the science and technology of cementitious materials used to immobilize nuclear waste. It summarizes the current knowledge in the field and highlights important areas that still need further investigation.

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