IAEA-TECDOC-1701

The Behaviours of Cementitious Materials in Long Term Storage and Disposal of Radioactive Waste

Results of a Coordinated Research Project

IAEA
International Atomic Energy Agency

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FOREWORD

Radioactive waste with widely varying characteristics is generated from the operation and maintenance of nuclear power plants, nuclear fuel cycle facilities, research laboratories and medical facilities. This waste must be treated and conditioned, as necessary, to provide waste forms acceptable for safe storage and disposal.

Many countries use cementitious materials (concrete, mortar, etc.) as a containment matrix for immobilization, as well as for engineered structures of disposal facilities. Radionuclide release is dependent on the physicochemical properties of the waste forms and packages, and on environmental conditions. In the use of cement, the diffusion process and metallic corrosion can induce radionuclide release. The advantage of cementitious materials is the added stability and mechanical support during storage and disposal of waste. Long interim storage is becoming an important issue in countries where it is difficult to implement low level waste and intermediate level waste disposal facilities, and in countries where cement is used in the packaging of waste that is not suitable for shallow land disposal.

This coordinated research project (CRP), involving 24 research organizations from 21 Member States, investigated the behaviour and performance of cementitious materials used in an overall waste conditioning system based on the use of cement — including waste packaging (containers), waste immobilization (waste form) and waste backfilling — during long term storage and disposal. It also considered the interactions and interdependencies of these individual elements (containers, waste, form, backfill) to understand the processes that may result in degradation of their physical and chemical properties.

The main research outcomes of the CRP are summarized in this report under four topical sections: (i) conventional cementitious systems; (ii) novel cementitious materials and technologies; (iii) testing and waste acceptance criteria; and (iv) modelling long term behaviour. The individual contributions of participating organizations and the overall conclusions of the CRP are also included.

CRP participants shared research and practices on the use of cementitious materials. Such exchange of information and cooperation in resolving common problems between different institutions in Member States contributes to improving waste management practices, including their efficiency and safety. The CRP promoted the exchange of information on ongoing research and development activities, and facilitated access to the practical results of the application of advanced waste management practices for the conditioning of specific types of waste. As a result of the CRP, new knowledge and practical experience will be transferred to Member States to improve their radioactive waste management practices.

This publication can serve as a screening tool to identify cementitious systems and technologies to meet specific waste management objectives in terms of the waste generated, the technical complexity of waste streams, the available economic resources, the environmental impact considerations and the desired end product (waste form). It can be used to compare cementitious systems and technologies in order to reach an informed decision based on safety, technological maturity, economics and other local needs.

The IAEA wishes to express its appreciation to all those who took part in the CRP for their contributions to the preparation of this publication, in particular F. Glasser (United Kingdom), C. Langton (United States of America), W. Meyer (South Africa), R.G. Yeotikar (India) and C. Cau dit Coumes (France). The IAEA officers responsible for this publication were Z. Drace and M. Ojovan of the Division of Nuclear Fuel Cycle and Waste Technology.

EDITORIAL NOTE

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1. INTRODUCTION

In the course of this coordinated research project (CRP), 24 research organizations from 21 Member States shared research and practices on the use of cementitious materials. The CRP facilitated the exchange of information and research cooperation in resolving similar problems between different institutions and contributed towards improving waste management practices, their efficiency and general enhancement of safety.

The objective of the IAEA CRP was to investigate the behaviour and performance of cementitious materials used in radioactive waste management system with various purposes. These included waste packages, waste forms and backfills as well as investigation of interactions and interdependencies of these individual elements during long term storage and disposal. Fundamental to this is an understanding of the processes that lead to the degradation of the barrier physical and chemical properties. The purposes of these elements in a waste management system are different, and thus the requirements for long term performance and account of degradation mechanisms /consequences may also be different. However all elements are important, as well as interactions envisaged between them, ultimately aiming to ensure the overall safety of a storage/disposal system.

Cement has many favourable properties, both chemical and physical, making it a desirable barrier or matrix for the encapsulation of radioactive and toxic wastes. Chemically cement has a high pH (e.g. its pore water) and forms hydration products which favour sorption and ion substitution. 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. Cement is also an inexpensive and readily available material, durable in its hardened state, fluid when initially cast and tolerant to a variety of waste forms, including those in solid and liquid states. Cements have also been proved to show their stability when irradiated and ability to act as radiation shielding.

Cementitious materials are widely used in waste management systems for many decades with different aims and requirements for their long term performance. Conventional cementitious materials such as Portland cement and Portland composite cements made with supplementary cementitious materials in the form of fly ash, iron blast furnace slag, silica fume, natural pozzolans, as well as novel cement systems such as geopolymers, high alumina and, calcium sulfoaluminate, as well as MgO based or phosphate (acidic) cements can be used to create reliable immobilizing elements for safe storage and disposal of wastes. These barrier functions, as well as interactions envisaged between various components, were considered in this CRP which was focused on predisposal management systems.

The predisposal waste management stage has as its objective the production of waste forms or waste packages suitable for storage, transportation and final disposal. Many countries use cementitious materials as a containment matrix for immobilization, as well as for engineered structures associated with storage and disposal facilities. Radionuclide release is dependent on the physical and chemical properties of the waste forms and waste packages and of the environmental conditions. Cementitious materials (waste forms, packages and backfills) are often used in form of composite materials, because of that transport mechanisms including diffusion processes are affected by the aggregate and metallic inclusion corrosion which can cause disruption and cracking of materials and lead to radionuclide release. On the other hand, cementitious materials contribute to mechanical stability and support at both storage and disposal stages. Long term interim storage is becoming an important issue in countries where it implementation of LILW disposal facilities is postponed and in others where cement is used in the packaging of waste not suitable for shallow land disposal.

Radioactive waste conditioning technology based on cementation has received considerable attention in the Member States in recognition of its importance for the protection of human health and the environment from adverse effects of radiation associated with release of radioactivity. During the evolution of waste management practices, many cementation processes have achieved a high degree of acceptance and many processes are now regarded as technically mature. A large body of information is currently available on these 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 did require improved material performance and technologies. Selection of waste conditioning technologies based on cementation for specific waste streams should always demonstrate waste safety and follow certain waste acceptance criteria for storage/disposal. Most safety criteria are well developed and are generally applicable to almost all waste management systems. Other criteria, e.g. waste acceptance criteria, could be waste, site or country specific. These requirements and associated criteria should therefore be carefully considered in development and application of cementitious materials in multipurpose packaging for transportation, long term storage and disposal. All these issues were within the scope of CRP and led to a subdivision of main tasks of its activities into several main streams.

The following specific research objectives were initially included in CRP: (i) cementitious materials for radioactive waste packaging: including radioactive waste immobilization into a solid waste form, (ii) waste backfilling and containers; (iii) emerging and alternative cementitious systems; (iv) physical–chemical processes occurring during the hydration and ageing of cement matrices and their influence on the cement matrix quality; (v) methods of production of cementitious materials for: immobilization into waste form, backfills and containers; (vi) conditions envisaged in the disposal environment for packages (physical and chemical conditions, temperature variations, groundwater, radiation fields); (vii) testing and non-destructive monitoring techniques for quality assurance of cementitious materials; (viii) waste acceptance criteria for waste packages, waste forms and backfills; transport, long term storage and disposal requirements; and (ix) modelling or simulation of long term behaviours of cementations materials used for packaging, waste immobilization and backfilling, especially in the post-closure phase.

The main research outcomes of the IAEA CRP are summarized in the report under four topical sections: (a) conventional cementitious systems; (b) novel cementitious materials and technologies; (c) testing and waste acceptance criteria; and (d) modelling long term behaviour, as well as conclusions of the overall CRP. These themes are further developed in the individual reports presented in appendices of this document. The individual contributions of participating organizations to CRP are also summarized in the main body of the document.

2. CONVENTIONAL SYSTEMS

Conventional systems for immobilization of radioactive waste consist of Portland cement, waste and water. The order of mixing is often important but in some cases is limited by the nature of the waste, e.g. infiltration of scrap by a fluid cement–water mix. Liquid and particulates are often homogenized with cement by stirring. In many applications a portion of the cement is substituted by a supplementary cementing material, e.g. fly ash or slag. After setting, the conditioned product can be transported and disposed in a facility. Apart from the cementitious waste products, cement is also used for construction of engineering barriers such as steel reinforced trenches, silos, etc. These, together with aspects of steel corrosion, have been addressed in this CRP.

2.1. PORTLAND CEMENT AND BLENDED PORTLAND CEMENT

Portland cement is produced worldwide to various national standards. These are, however, similar worldwide. The product is marketed as a free flowing powder with a high specific surface ~2000 cm^2/g or more. The product is perishable and must be stored in recommended conditions. The manufacturers have rigid quality assurance regimes so the as supplied product will be documented. The main use of Portland cement is, however, in construction and the specification and QA are appropriate to these uses: the nuclear industry may require additional QA criteria.

When cement powder is mixed with water, the mix has an initial period of fluidity during which it can be mixed, pumped, poured or infiltrated. This period usually lasts several hours. Thereafter, the mix loses fluidity, although strength gain occurs more slowly and is usually only measureable after 12–24 hours. The set process can be affected by water soluble substances as well as by flocs and colloids. Set and strength gain can be affected by added substances: both accelerators and retarders are known. Indeed, the commercial product normally contains some (a few wt.%) added calcium sulphate, as gypsum, hemihydrate or active anhydrite, to ensure a period of workability.

TABLE 1. MAIN CRYSTALLINE PHASES OF UNHYDRATED PORTLAND CEMENT

Cement Nomenclature	Actual Formula	Name	Mineral Phase
C_3S	$3\ CaO \cdot SiO_2$	Tricalcium silicate	Alite
C_2S	$2\ CaO \cdot SiO_2$	Dicalcium silicate	Belite
C_3A	$3\ CaO \cdot Al_2O_3$	Tricalcium aluminate	Aluminate or Celite
C_4AF	$4\ CaO \cdot Al_2O_3 \cdot Fe_2O_3$	Tetracalcium alumino ferrite	Ferrite

The four compounds present in Portland cement, abbreviated C_3S, C_2S, C_3A and C_4AF, (C=CaO, A=Al_2O_3, S=SiO_2 and F=Fe_2O_3) are the main crystalline phases of Portland cement.

The cement powder is itself not homogeneous. It consists (>95%) of the four substances shown in Table 1. The industry varies the proportions of these phases to influence the strength gain and increase resistance of the hardened product in subsequent service to attack by soluble sulphate. For example, the early strength of cement is usually increased by increasing the proportion of tricalcium silicate while the resistance to sulphate attack is enhanced by reducing the content of tricalcium aluminate. Finally, the content of calcium sulphate additive is regulated to control set time and shrinkage.

Because manufacturers supply only a few types of cement, the properties are conventionally modified by means of admixtures and blending agents. The terminology used is not universally agreed but the definitions shown in Table 2 will be adopted here.

TABLE 2. CLASSIFICATION OF MATERIALS ADDED TO PORTLAND CEMENT

Designation	Examples and purpose
Aggregate	Inert particulate or granular minerals added as fillers. They dilute the heat of hydration and reduce shrinkage in the course of hardening.
Admixtures	Chemicals added to control the properties of cement in the fluid state. They may be either inorganic or organic, e.g. water dispersible organic plasticisers or powdered limestone. Normally comprise <5% by mass.
Blending agents	Inorganic materials reactive with cement in the longer term and contributing to matrix formation. Examples include slag, fly ash and silica fume. Normally added up to 66% (fly ash) or exceptionally 90% (slag).

Naturally, the relatively high content of blending agents can affect the physical and chemical properties of the matrix. The literature and experience of civil engineering is a good guide to optimization of the performance of such matrices.

Additionally, the nuclear industry may add selective sorbers for radionuclides to the cement formulation. These are intended to increase the binding power for selected nuclides, e.g. Cs. Examples of substances added for this purpose include zeolites, bentonite and vermiculite.

The hydration process of Portland cement proceeds spontaneously, even under water, hence Portland cements are termed “hydraulic” cements. All that is necessary to achieve strength is to leave the fresh mix undisturbed. The mix water content is, however, crucial to obtaining a strong and durable matrix. This is usually expressed as a water to cement weight ratio (w/c). Plasticity generally requires a w/c ratio >0.35 but this ratio can be increased to nearly 1.0 and still get a hardened product, albeit it will be rather porous. But problems develop at high w/c ratios: the denser components may segregate and liquid water (known as laitance) may appear; strength will reduce and porosity and permeability increase.

Much of the water added to cement becomes chemically combined into hydrate solids. Thus cement gains strength not by drying but by chemical combination. The critical w/c ratio which, if exceeded, will leave unconsumed water, is ~0.3–0.35. Any unconsumed water remains trapped in pores and gives rise, for example, to a “pH”. Strictly, the pH reported is not that of cement but of the pore fluid. Pore fluid can be extracted from hardened cement by expression in a powerful hydraulic press and its characteristics determined. Modern cements will reach 80–90% hydration in 30 days and almost complete hydration within a year.

2.2. PROPERTIES AND SELECTION OF CEMENT

The properties of cements have been extensively studied by civil engineers and a large body of national specifications exists for the measurement of parameters such as compressive and flexural strength. When formulating cement mixes, these specifications and good practice guides should always be consulted. However many properties useful in nuclear applications are not so readily measured: for example, porosity and permeability. In measuring these parameters, it is important to reference the procedures used but if this is not possible, or if the method is novel, benchmarking measurements should be included. The testing and quality assurance of cements will also be described in another section.

It is also noteworthy that cements are used in many engineering applications as composite materials. Hardened Portland cement is weak in tension and, to counteract this, steel (or other) reinforcement is used. The reinforcement may be plain or tensioned: both pre- and post-tensioning methods are regularly used in civil engineering. Thus the selection of a cement matrix formulation may have to be optimized with respect many parameters including interactions with other embedded materials, to waste loading, etc. Much of the following text gives practical examples of optimization of processing and formulation for a broad spectrum of specific waste streams but it is not possible to evaluate every application: there is no substitute for a thorough understanding of the properties of cement especially as the quality is often determined by formulation and handling.

2.3. METHODS OF CEMENT WASTE PRODUCT (CWP) PREPARATION

2.3.1. CWP preparation in the laboratory

The components of a CWP are complex. Thus the main variables in optimization of cement matrix are

- Waste;
- Water to cement ratio;
- Waste to cement ratio;
- Admixtures (type, content);
- Admixture to cement ratio;
- Type of cement;
- Order of mixing;
- Emplacement and curing.

In process optimization, it is usual to change one variable at a time. The formulation is made in a suitable container with the requisite quantity of waste, cement and water (if required), are added. The order of addition is often important to ensure a homogenous product. Using liquid and particulate wastes, the mixture is homogenized perhaps using a mechanical stirrer. The stirrer is removed and the CWP is allowed to set undisturbed for a few days. Thereafter the CWP may be removed from the container and curing continued in a humidity chamber at ~100% RH or under water. After complete curing, nominally achieved in 28–90 days, the monolith can be used for leaching and compressive strength measurements, etc.

2.3.2. Cementation at plant scale

Three types of cementation process are used for cementation of various types of liquid wastes. These are:

In drum/container cementation: In this process the components including waste are mixed in a standard 200 L drum with a disposable or removable stirring unit. After setting and hardening, the CWP drum is closed by a lid and sent for disposal to a NSDF (Near Surface Disposal Facility).

Cementation using a mixer unit: In this method, the cement and waste are mixed and, when homogenized, poured into a standard 200 L drum or in a container. The drum / container is closed and, after strength gain, disposed into a near surface disposal facility (NSDF).

In situ cementation: Cementation of waste is often done at large scale: for example in India 4000 litre capacity cylindrical conditioning tanks are used. The conditioning tanks are installed in Reinforced Concrete Construction (RCC) trenches on a layer of vermiculite. The conditioning tanks are interconnected at a certain level to take care of overflow. The conditioning tanks are equipped with a disposable stirring assembly and an opening for addition of cement. All the tanks in the RCC trench are also interconnected to an exhaust system; a separate exhaust system is in the process of being installed with a cyclone separator, filters and blower. Since immobilization in cement is carried out inside the conditioning tanks, this process is termed "in situ cementation". In situ cementation is widely used, as for example in the USA, where very large tanks and silos up to several million L have been cement filled with low strength grout.

2.4. CEMENTITIOUS SYSTEMS FOR WASTE IMMOBILIZATION STUDIED DURING THE CRP

Cement matrices have been used for immobilization of various types of wastes. These CWPs are primarily evaluated for compressive strength and chemical durability. Other characterization procedures include (i) phase identification by XRD, (ii) porosity, (iii) water resistance, (iv) freeze–thaw resistance, (v) flowability, (vi) heat generation, (vii) loading of salts. The types of waste and waste matrix are shown in Table 3.

TABLE 3. EXAMPLES OF CONVENTIONAL CEMENTITIOUS FORMULATIONS

Waste Stream	Cementitious Matrix*
Spent ion exchange resins	Slag–Portland blends
Sludge and concentrates generated from treatment of LLW	OPC, with or without additives
Mixture of sludge and ion exchange resin	OPC, Slag–Portland cement
Intermediate level liquid waste	Slag–Portland blends, OPC with vermiculite
Secondary waste generated during treatment of spent solvent from reprocessing plant	OPC
Waste generated during reprocessing of thorium based spent fuel	OPC
Evaporator concentrate containing boric acid	OPC

*"Admixture" includes supplementary cementing materials such as slag or fly ash

2.5. APPLICATION EXAMPLES

2.5.1. Immobilization of spent ion exchange resins

Ion exchange resins are widely used for decontamination of water such as of reactor coolants, e.g. ion exchange columns used for decontamination of coolant water from Pressurized Heavy Water Reactors (PHWR) containing mixed resins of strongly acidic ($R-SO_3H$) cationic as well as strongly basic ($R-CH_2-N(CH_3)_3OH$) anionic forms used in 30:70 weight ratio. Typically ^{137}Cs and ^{60}Co are the major radioactive nuclides to be removed from solutions. An example of application of cements for ion exchange resins immobilization is that from India. Although spent ion exchange resins are currently immobilized in a polymer matrix in India, Slag Based Cement (SBC) was developed as an alternative. The slag cement, together with resin and adequate water, were prepared. The CWP matrix had properties listed in Table 4 (See Appendix, India) and was acceptable with respect to compressive strength and chemical durability.

TABLE 4. PROPERTIES OF CWP WITH ION EXCHANGERS

Ion Exchange Resin	Waste to SBC ratio	Bentonite (% of cement)	Vermiculite (% to cement)	Water to cement ratio	Compressive strength (MPa)	Leach rate (g/cm^2d)
Mixed cationic: anionic 30:70	0.8: 1	4.4 to 8.8	4.4	0.7:1	4.96 to 5.63	6.5 x10^{-4}
Mixed cationic: anionic 20:80	0.65: 1	3	4	0.5:1	5.5 to 6.3	8.4 x10^{-5}
Mixed cationic: anionic 20:80	0.65: 1	3	3	0.35:1 +0.5% Super plasticiser	5.5 to 6.3	7.8 x 10^{-5}

2.5.2. LLW sludge

Sludge resulting from the chemical treatment of radioactive liquid effluents is normally immobilized in cement matrices with or without additives. Radioactive effluents containing complexing agents such as oxalic and citric acids are generated during chemical decontamination operations. The presence of these complexing agents can change the properties of the CWP and an upper limit for their loading may be imposed. The study was carried out with the normal cement and concrete compositions with and without mineral additives (bentonite and volcanic tuff). The CWP was prepared with non-active sludge components (iron, as hydroxides and phosphate, calcium phosphate and copper ferrocyanide) and non-active organic acids and salts (oxalic, citric, tartaric). Pozzolanic additions cause changes to the hardening properties of the cement matrix, depending on the proportions used Pozzolanic reactions of bentonite and tuff consume calcium hydroxide, converting it to (mainly) calcium silicate hydrogel (CSH). Thus after hydration, calcium hydroxide is found in lower proportions than in normal Portland cement pastes. The composition of CSH probably has a lower C/S than the CSH of Portland cement pastes. Compressive strengths obtained on cubic specimens made from cement–bentonite–water (1:0, 1:0,5) and cement–volcanic tuff–water (1:0, 1:0,5) are similar to those obtained for reference matrix formulated with Portland cement, so these mineral additives do not affect the strength of the cement matrix. The evolution of compressive strength in cubes containing organic acids has been determined and is similar to that of the reference cement matrix. Oxalic acid, however, decreases the permeability of concrete; it reacts with cement forming insoluble calcium oxalate (hydrate), which clogs pores and cracks, so developing a good physical structure. Following 10 years trench burial, the results obtained for conditioning matrix with various additives is within acceptable limits. Some of the laboratory and actual field test specimen data are given in Table 5 (See Appendix, India).

TABLE 5. PROPERTIES OF CWP WITH ORGANIC ACIDS

Sample	Compressive strength (N/mm^2)				
	1 year	3 years	5 years	7 years	10 years
Cement–Water laboratory conditions	28.3	51.3	61.0	64	49,8
Cement–Water in a disposal facility, at position 1	39.5	55.3	63.5	69	NA
Cement–Bentonite–Water, laboratory conditions	NA	NA	*36.25*	*36.3*	*37.1*
Cement–Bentonite–Water, in a disposal facility, at position 2	NA	NA	*36.5*	*36.5*	*40.97*
Cement–Oxalic acid laboratory conditions	NA	NA	*57.5*	*NA*	*85.95*
Cement–Oxalic acid in a disposal facility, at position 1	NA	NA	*67.25*	*NA*	*114.62*
Cement–Citric acid laboratory conditions	NA	NA	*67.5*	*NA*	*83.36*
Cement–Citric acid in a disposal facility, at position 1	NA	NA	*71.25*	*NA*	*74.2*

NA =Data not available. Positions 1 and 2 are sampling points.

2.5.3. Liquid ILW

Liquid ILW is generated at the reprocessing plant during concentration of HLW. The waste is initially acidic but has been neutralized to raise the pH above 9 for storage in carbon steel tanks. This results in an increase of dissolved solid content. Ordinary Portland Cement (OPC) and Slag Based Cement (SBC) formulations were used for preparation of CWP in the laboratory for finalization of the composition to be used at plant scale. The OPC based formulation with added vermiculite was adopted for in situ immobilization of ILW in the underground conditioning tanks (capacity 4000 litres) located in RCC trenches. Properties such as compressive strength and stabilized leach rate were determined on CWP cores drilled from the conditioning tank. These were compared with laboratory data for quality assurance purpose. Some of the data are given in Table 6 (See Appendix, India).

TABLE 6. COMPARISON OF CWP CONTAINING ILW

Block details	Laboratory scale CWP preparation		Plant scale CWP preparation		
			CWP-1 (28 days cured)*	Core drilled sample-1	Core drilled sample-2
Cement formulation	OPC + 20% vermiculite	SBC	OPC +20% vermiculite		
Parameters					
Waste : Cement proportion	1:1.3	1:2	1:1.3	1:1.3	1:1.3
Weight, gm	24.10	28.99	257	80	83
Total βγ activity in the block, MBq	12.78	12.78	91.21	30.08	37.84
Compressive strength, MPa	4.0–4.5	4.0–4.5	3.5–4.0	3.5–4.0	3.5–4.0
Leach rate (stabilized after 100days) on activity basis, $gm/cm^2/d$, x 10^5	1.25	2.01	0.94	1.23	1.00

*This CWP was prepared using slurry taken from the conditioning tank and cured.

2.5.4. Secondary waste generated during treatment of spent solvent from reprocessing plant

Spent solvent organic waste (30% tri-butyl-phosphate after dilution) is generated from reprocessing plants. An alkaline hydrolysis process has been adopted for its treatment. This leads to the recovery of the diluent, virtually free of activity and an alkaline aqueous waste in emulsion form. A cement matrix has been developed and adopted on the plant scale for immobilization of this waste using OPC with waste to cement ratio of 1:1.5 (See Appendix, India). Details of the CWP block are given in Table 7.

TABLE 7. PROPERTIES OF CEMENTED TBP WASTE

Parameters	Value
Weight (g)	231
Total activity in the block (MBq)	1.887
Compressive strength , MPa	5.8
Leach rate after 30 d on gross beta loss basis ($g/cm^2/d$)	2.8×10^{-4}

CWP for liquid waste generated during reprocessing of irradiated ThO_2-fuel rod.

During reprocessing of ThO_2 containing fuel rods, irradiated in the reactor, a radioactive liquid waste stream containing Th, Al and F is generated. Process development studies were conducted for immobilization of this type of waste using OPC with waste to cement ratio of 1:1.5 and compatibility was established. Leaching data of two active CWP blocks on the basis of gross β, γ is given in Table 8 (See Appendix, India).

TABLE 8. LEACH RATIOS OF CEMENTED THORIUM FUELS

Time in Days	LR (g/cm^2.day)*	LR (g/cm^2.day)
1	3.121 x 10^{-2}	3.48 x 10^{-2}
2	1.919 x 10^{-2}	2.235 x 10^{-2}
3	1.102 x 10^{-2}	1.560 x 10^{-2}
4	8.1 x 10^{-3}	9.825 x 10^{-3}
11	5.15 x 10^{-3}	6.984 x 10^{-3}
18	4.523 x 10^{-3}	4.82 x 10^{-3}
25	3.097 x 10^{-3}	4.432 x 10^{-3}
32	1.12 x 10^{-3}	2.385 x 10^{-3}
40	7.502 x 10^{-4}	8.899 x 10^{-4}
46	5.01 x 10^{-4}	6.465 x 10^{-4}

* LR = Leach Rate

2.5.5. Cementation of sludge and old pulp waste

Cementation of old pulps is a difficult technological task because of their complicated chemical composition; they contain hydroxides of manganese, iron, nickel, etc., as well as silicon oxide, and are characterized by a relatively high activity. The research of cementation of these pulps included the study of the impact of sorbing additive type and content on cement compounds leachability, flowability, and the impact of cement composition on its mechanical strength after ageing, heat generation of cement compounds and other factors. Investigations were performed using simulate solutions and pulps containing radionuclides. Portland cement and slag Portland cement with sorbing additive (clinoptilolite or bentonite) may be used as a matrix material. Optimized product composition and properties are shown in Table 9 (See Appendix, Russian Federation, VNIINM). The next step would be testing prior to implementation in an industrial cementation facility. A pulse type mixer was developed at A.A. Bochvar's Institute in the Russian Federation. The facility does not use any stirrer and the homogenized cement compound is discharged from the mixer.

TABLE 9. PROPERTIES OF CEMENTED PULP WASTE

Composition of hydrated salt sludge, g/l			Composition of compound, % by mass		S/C*	W/C**	Loading capacity, % by mass	Flowability of cement compound, mm	Mechanical strength of cement compound [σ_{comp}]	
$Fe(OH)_3$	Na_2SO_4	$NaNO_3$	Pulp	Binder					Time, days	[σ_{comp}], kg/cm^2
30	30	240	59.5	40.5	1.47	1.1	15.0	120	28 51 360	35 32 45
30	30	240	57.1	42.9	1.33	1.0	14.1	110	28 51 360	34 40 55
30	30	240	54.5	45.5	1.2	0.9	13.6	90	28 330	52 95
15	15	270	54.5	45.5	1.2	0.9	13.6	140	32 63 159	32 49 73
15	15	270	40	60.0	0.67	0.5	10.0	70	28 56	155 169

*S/C –ratio of waste in the cement compound mass to the matrix material mass.
**W/C – the ratio of the water mass in the cement to the matrix material mass.

2.5.6. Cementation of high saline liquid radioactive waste (LRW) and miscellaneous wastes

Development of cement compositions was carried out for different types of radioactive waste such as saline LRW (content of $NaNO_3$ up to 90%), concentrated boron containing saline LRW, LRW with high surface active substances content, liquid organic radioactive waste, spent ion exchange resins and filter bed "perlite" powder, ash residues from solid radioactive waste (SRW) combustion, a mixture of closely packed and large fragmented SRW. The basic aim of this study was finalization of equipment parameters, methods and cement and grout formulations for maximum waste loading. The CWPs were evaluated for various physical–chemical properties using several methods such as derivatographic, X ray, petrographic, microscopic and autoradiographic analyses. Laboratory tests were based on standard and specific methods (methods of determination of leaching of macro components and radionuclides, freeze–thaw resistance, resistance to water and radiation damage. Mathematical regression and statistical analysis of experimental data were performed. An analysis of technological factors was done based on pilot plant testing and industrial tests of RAW cementation in different conditions at plants and with different equipment (see Appendix, Russian Federation, RADON). The cement grout preparation parameters were determined to find LRW cementation conditions by the mixing method, which included acceptable quality of mixing, permissible variation of water/cement ratio (±ΔW/C), solution/cement ratio (±ΔS/C) of the specified formulation, and its setting time and spreadability.

Optimum preparation parameters of cement grout were defined for the following plants and technological processes including an intermittent cycle system for preparing cement in the container designed for process reliability. The system uses standard 200 l drums with a disposable frame mixer. Cement mixture is added into the drum with subsequent addition of LRW to the prepared cement mixture. Two types of multi-component compositions for liquid and solid RAW were developed, as dry mixes suitable for usage in a single technological step. Variable proportions of two are used depending on the type of waste.

The cement composition for LRW contains PC 85–95 %, bentonite clay 5–15 %, antifoam agent 0.1–0.5 %. When boric acid concentration are in excess of 20–25 g/l about 40 % of $Ca(OH)_2$ is also added to the composition. For fine dispersed SRW the cement composition contains PC 96–98 %, bentonite clay up to 2 %, stabilizer 1–2 %, plasticizer up to 2 %. Precise formulation of cement composition depends of the RAW type and technological processes prevailing at the site. Results of experiments on spreadability for $NaNO_3$ solution are shown in Fig. 1.

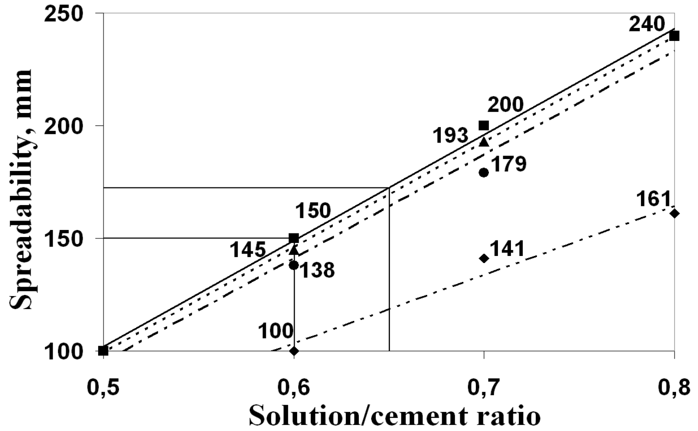


FIG. 1. Spreadability of fresh mixes, mm of slump Numbers on the figure refer to mixe designations. Spreadability relation of cement grouts of composition: water, portland cement, bentonite (■), solution of $NaNO_3$ with concentration of 300 g/l, PC, bentonite (▲), LRW of SUE SIA "Radon" with concentration of 250 g/l, PC, bentonite (•),LRW of Kalinin NPP with concentration of 500 g/l, PC, bentonite (♦) of the solution/cement ratio.

2.5.7. Evaporator concentrate and ion exchange resin containing boric acid

The study was carried out for the immobilization of evaporator concentrate containing borate and ion exchange resins in a cement matrix and evaluation of its long term stability (see Appendix, Sweden). It was found that when the concentration of boric acid is about 4 wt % in a cement–waste matrix the matrix does not solidify. The compressive strength for cement specimens containing artificial evaporator concentrates also decreases with increasing total salt concentration. It was observed that the compressive strength of cement–waste matrices containing boric acid increases during the first 6 months after casting. The curing curve for the boric acid concentrate and the cement is given in Fig. 2.

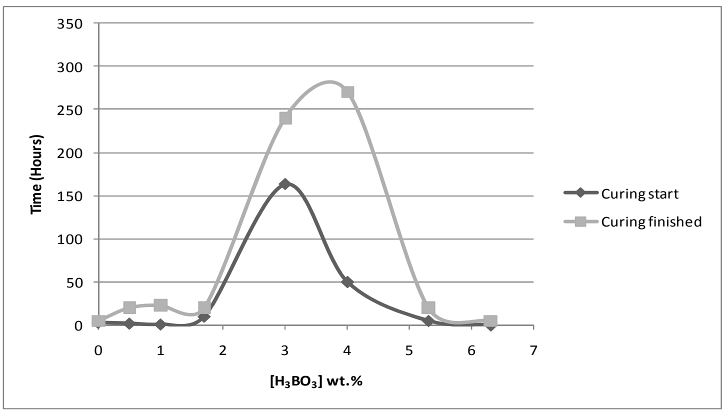


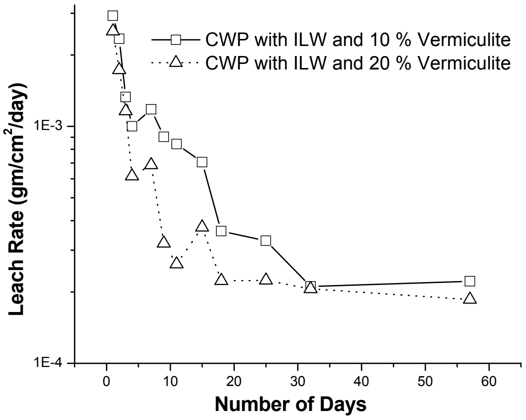
FIG. 2. Impact of borate waste content on time to initial and final set.

2.6. IMPROVEMENT OF CWP

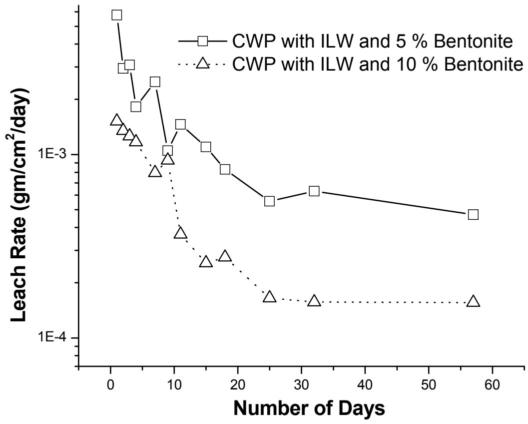
Development of the cement matrix is required depending on the waste composition. The development is aimed at improving the product properties and/ or process. Backfill or additives can give improved cement waste products (CWP).

2.6.1. Addition of sorbers

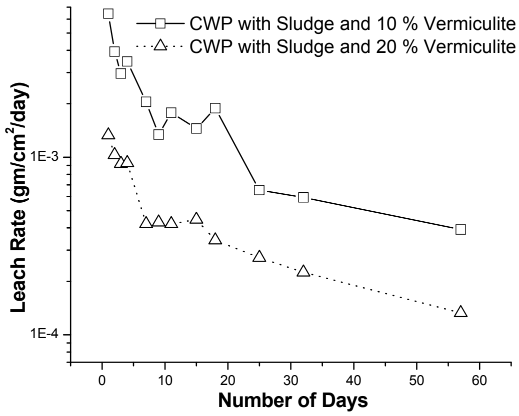
Sorbing materials including vermiculite and bentonite, were incorporated in the OPC matrix during preparation of CWP in the laboratory. The waste types selected were (a) alkaline ILW, (b) sludge from chemical treatment of LLW, (c) spent resorcinol formaldehyde polycondensate (RF) resin and (d), spent styrene divinyl benzene based anion and cation mixed bed resins. The OPC to waste ratio was fixed at 1.3:1 weight to volume. The amount of additives was varied. These products were evaluated for compressive strength and leachability. The CWP prepared from OPC and various waste form and additives were quite good and have comparable compressive strengths. In general, the CWPs prepared from various waste compositions with vermiculite as an additive were more durable with respect to leaching. Increasing the amount of vermiculite has also given better results. This is due to trapping of Cs by the vermiculite and its subsequent immobilization. Amongst the waste compositions, CWP made for RF resin gave a lower leaching rate in the presence of vermiculite and bentonite. This is due to highly specific nature of RF resin for trapping Cs. It was also observed that an increase in either vermiculite or bentonite in CWP made with RF resin had not given any improvement with respect to leaching. This could be due to trapping of Cs activity by RF resin itself. The leach rate data presentation for CWP for immobilization of ILW and sludge after incorporation of vermiculite and bentonite are given in Fig. 3.



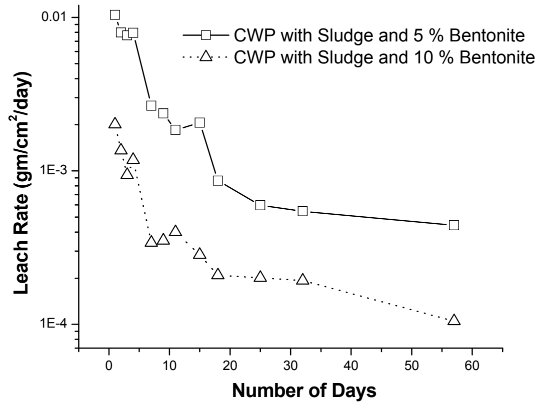
Leach rate of CWP prepared from ILW with various concentrations of Vermiculite



Leach rate of CWP prepared from ILW with various concentrations of Bentonite



Leach rate of CWP prepared from sludge with various concentrations of Vermiculite



Leach rate of CWP prepared from sludge with various concentrations of Bentonite

FIG. 3. Influence of additives on the leach rate of cemented waste forms.

2.6.2. Solidification of difficult waste streams

The durability of concrete is an important issue and its assessment plays a major part in understanding the characteristics of concrete. The ability of concrete to withstand the penetration of liquid and oxygen contribute to its durability. The durability of concrete, can in turn, be quantified by certain characteristics such as the porosity, sorptivity and permeability. To improve the characteristics of current grout/cement matrixes used for the encapsulation of radioactive waste, different cement mixtures made with CEM 1 (96% OPC) and CEM 5 (mixture of 20% fly ash, 20% blast furnace slag and 60 % Portland cement powder) with the addition of different admixtures, inert fibre material and plasticizers were investigated. With no formal guidance from the WAC of the disposal site, it was decided that the following matrix requirements have to be met in order to qualify a possible matrix for radioactive waste immobilization. Results with radioactive waste (excluding organic waste) indicated an admixture of bitumen or asphalt in CEM 1 (96% OPC cement) has the best characteristics and complies with the specified requirements.

Treatment of contaminated organic waste which is a non-standard waste stream proved to be difficult because many organic liquids are immiscible with water. Cementation is generally not an option as the cement matrix binds poorly with the organic phase. The absorption of organics such as TBP and oil onto" Nochar" polymer systems has been demonstrated to be successful with no loss in activity (See Appendix, South Africa). It has also been demonstrated that after the encapsulation of the polymer (absorbed with organics such as oil or TBP) into the selected cementitious grout, no leaching of radionuclides were observed. The tensile and compression strength of this matrix was improved with the addition of the organic matrix as well as PVA fibres. The summary of the study is given in Table 10 (See Appendix, South Africa).

TABLE 10. TREATMENT OF "DIFFICULT" WASTES

Waste Type	Composition of grout matrix used at Necsa
Graphite fuel spheres	CHEM 1 with asphalt additives
Sludge	CHEM 1 with asphalt additives
Resins	CHEM 1 with asphalt additives
Liquid	CHEM 1 with asphalt or vermiculite as additive
Tritium	CHEM 1 with asphalt additives with bitumen coating
Organics (oil/TBP)	CHEM 1, nochar absorbent, asphalt additives, fibres.
Graphite dust	Cold ceramic as precursor into CHEM 1 with asphalt additives
Tc and I waste	Cold ceramic as precursor into CHEM 1 with asphalt additives

2.6.3. Incorporation of additives

The study for improving cement waste product to achieve lower leaching was carried out by incorporation of clay and synthetic zeolite-A (see Appendix, Egypt). The clay concentration was varied from 5–20 wt.% at water/cement (w/c) ratio of 0.4. Zeolite cement matrices were prepared with a water/cement (w/c) ratio of 0.35, with different zeolite A loadings at 2, 4, 6, 8 and 10 wt.%. Incinerator ash–cement matrices were prepared by mixing plain OPC with 6, 12, 20 and 30 wt.% of ash at different water to cement–ash ratios. The CWP blocks were evaluated for compressive strength and leaching characteristics. It was found that the compressive strength of the clay–cement solidified matrices have the highest value at 10 wt.% clay addition. The results of the compressive strengths of the hardened cement pastes and cement pastes mixed with different percentages of synthetic zeolite A, at 0.35 w/c ratio, indicated that that increasing the ratio of the zeolite and incineration ashes decreases the mechanical strength of the sample. It was observed that incorporation of clay additives on the cumulative leach fraction (CLF) of ^{137}Cs was less than 5% for each of the studied cases. The addition of 10% clay decreased the CLF for the studied radionuclides. The CLF from OPC bentonite waste matrix is lower than that from OPC red clay. There was a decrease in CLF when 4% zeolite A was added. Similar decreases in CLF were obtained with increased ash loading. The leaching curves describing the cumulative leach fractions of ^{137}Cs, radionuclides from different cement based waste matrices are presented here (Fig. 4).

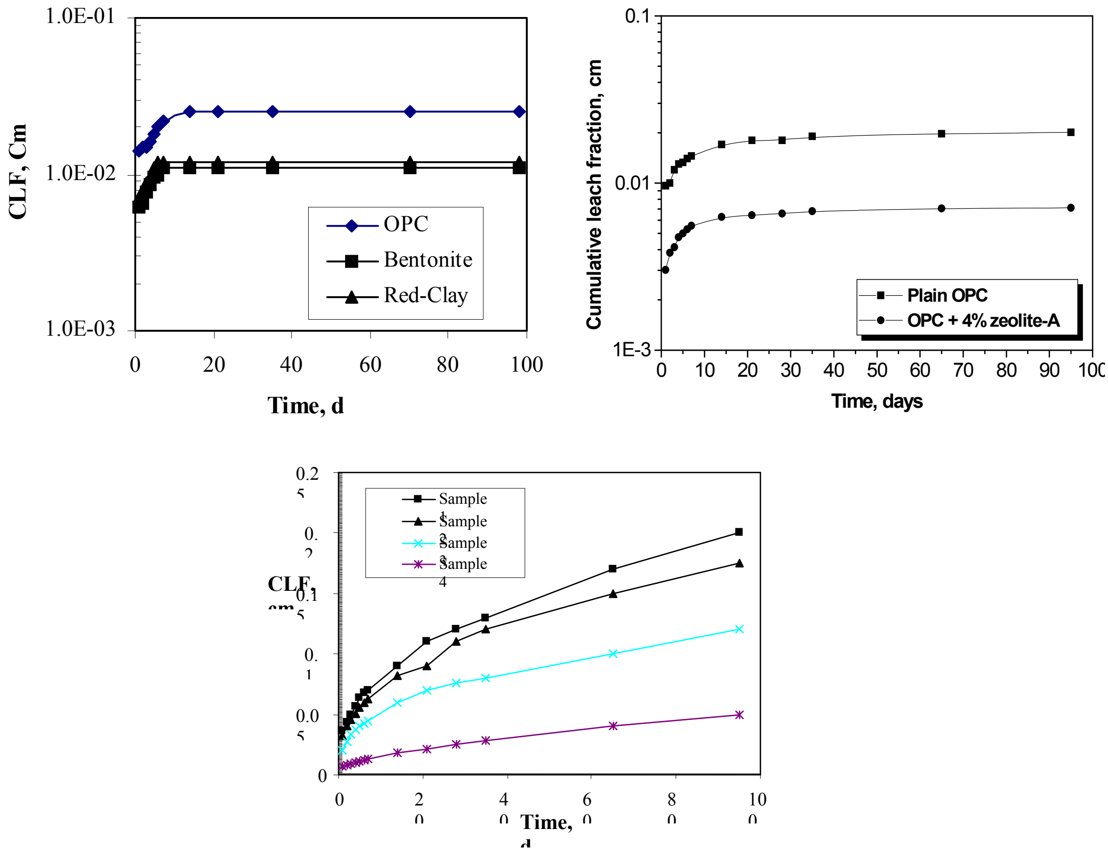


FIG. 4. Cumulative leached fraction from modified cement matrices.

2.7. ASSESSMENT OF A SILO CONCEPT

Near surface silo type disposal systems have been planned in several countries e.g. Sweden, and are at various stages of design, construction and operation phase. The concept of a disposal silo is illustrated in Fig. 5.

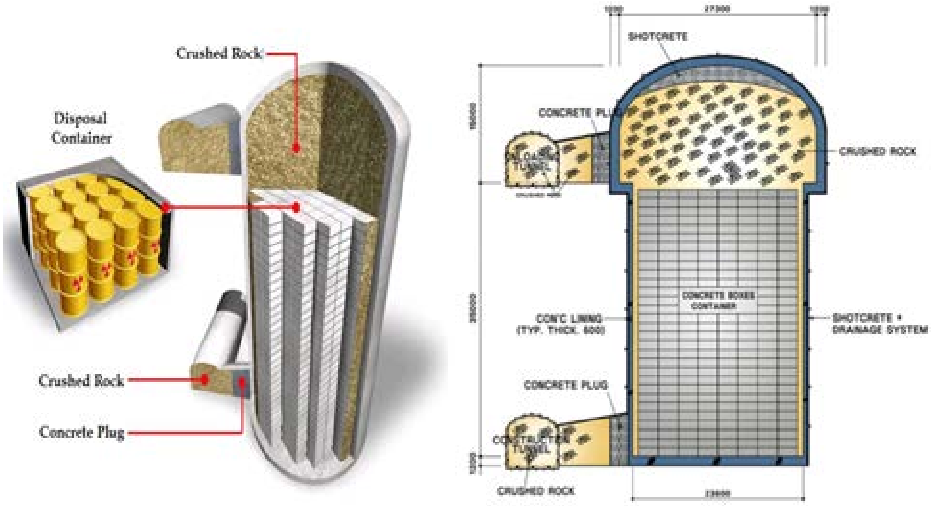


FIG. 5. Concept of disposal silos at the Wolsong LILW Disposal Center in the Republic of Korea.

Concrete silos are intended to contain waste packages, disposal containers and a backfill. The use of cementitious backfill materials for closure of silo was investigated. For example, the Slovenian national agency for radwaste management (ARAO) in 2009 adopted a national plan for a low and intermediate level waste (LILW) repository at Krsko. The selected option was to construct a near surface facility comprised of a silo placed in the saturated aquifer composed of silt with lenses of sand or clay and which extends a few hundred meters deep. Due to challenging geological conditions the LILW repository relies on the engineered barriers. Therefore a study of different cementation materials was made to find sustainable materials for engineered barriers in the repository (silo, backfilling, concrete containers, etc.), assessment of possible degradation processes and a methodology for the selection of appropriate locally available materials and their combination which can diminish some of the degradation processes.

The research was focused on the investigation of four concrete compositions and their characteristics (workability, compressive strength), durability analysis (resistance to penetration of water, freeze/thaw resistance, resistance to groundwater), rheology of concrete (heat of hydration, autogenous and concrete shrinkage), protection ability to prevent corrosion of reinforcement and numerical simulation of degradation processes in the cementation materials. Tested cementation mixtures require improvements in the formulation of binder compositions. The evaluation of four cement compositions for compressive strength is given in Fig. 6.

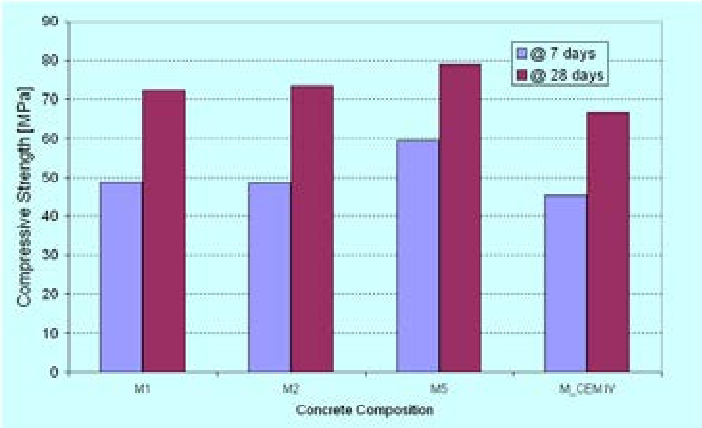


FIG. 6. Results of compressive strength measurements for 4 compositions for 2 time periods.

Characterization of cementitious materials, development of silo closure concept, and evaluation of long term behaviour of cementitious materials, including concrete degradation in repository environment were carried out in Republic of Korea. The investigation comprises performance testing of the physico–chemical properties of cementitious materials, degradation modelling of the concrete structure, comparison of performance for silo closure options, radionuclide transport modelling, taking into account concrete degradation at the site, and implementation of a parameter database for quality assurance and safety/performance assessment. Corrosion of reinforcement steel induced by chloride attack and degradation of concrete was studied and modelled. Electrochemical experiments were conducted to investigate the effect of dissolved oxygen, pH, and Cl^- on the corrosion rate of reinforcing steel in a concrete structure saturated with groundwater. Laboratory scale experiments and thermodynamic modelling were performed to determine the porosity change of the OPC cement pastes.

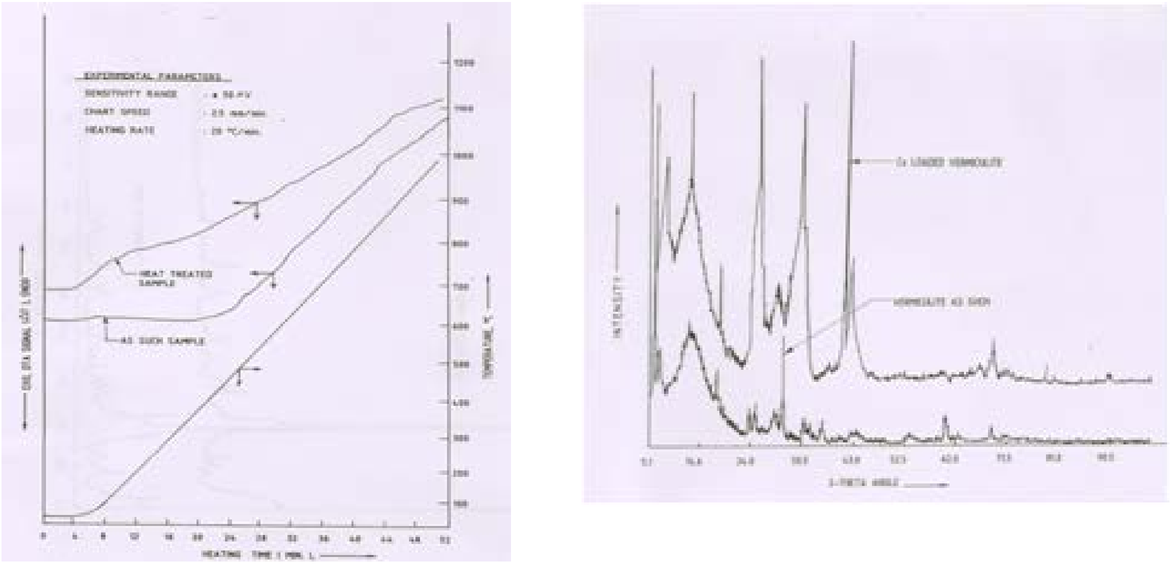
2.8. BACKFILL, ADDITIVES AND ADMIXTURE

Additives to waste are most commonly used to absorb activity present in the aqueous phase to improve retention of radioactivity in solid forms including tobermorite-like CSH gel. Admixtures are mixed with cement and sorption of radioactivity in liquid phase occurs concurrently with cement setting. Two types of admixtures are commonly employed for modifying the properties of CWPs to suit the chemical and physical characteristics of waste.

2.8.1. Inorganic admixtures

2.8.1.1. Vermiculite

Vermiculite is an aluminosilicate clay formed in nature from the degradation of mica. It has caesium specific sorption properties. DTA of vermiculite indicate that it is thermally stable under conditions likely to be encountered in a cement conditioned repository. To understand the structural change occurring in vermiculite after Cs absorption, the vermiculite was loaded with Cs and evaluated by X ray diffractometry (XRD). The XRD analysis of the Cs loaded vermiculite shows different peaks indicative of the structural change. This specificity for irreversible sorption of caesium is most important for blending with cement. There is structural change in vermiculite after Cs absorption: the DTA and XRD spectra of vermiculite are given in Fig. 7.



DTA run of heat treated and as such vermiculite | XRD pattern of Cs loaded and as such vermiculite

FIG. 7. Thermal analysis and powder diffraction of vermiculite before and after Cs loading.

2.8.1.2. Bentonite

Bentonite as an admixture widely studied due to its sorption properties for radioactive cesium, strontium and actinides. Bentonite exhibits special properties of plasticity and swells in the presence of water. Possible disadvantages of incorporating bentonite into cement are a reduction of strength of the cement matrix and increasing w/c ratio. When used as a cement admixture, its swelling capacity is reduced but despite the generally increased water to cement ratio, bleeding decreases. The swelling of bentonite is of the order of 200–280 %. Properties and compositions of vermiculite and bentonite admixtures are given in Table 11 (See Appendix, India).

TABLE 11. PROPERTIES AND COMPOSITIONS OF VERMICULITE AND BENTONITE ADMIXTURES

Item	Vermiculite	Bentonite
Size	-30 + 70 Mesh	90 % should pass through 200 mesh
True density (gm/cc)	2.6–2.7	2.4–2.6
Cation Exchange Capacity (meq/100gm)	40–50	70–100
Chemical Composition		
SiO2 (%)	35–40	45–55
Al2O3 (%)	10–12	15–20
Fe2O3 (%)	6–8	3–6
MgO (%)	20–25	3–4
Na2O (%)	---	1–2
H2O (%)	10–15	10–15
Swelling (%)	20–50	100–250
Porosity (%)	50–60	40–60

2.8.1.3. Silica fume, precipitated silica and glass powder

Silica fume is a by-product of silicon preparation. Its high surface area is attractive for use as a reactive admixture in CWP. It forms additional calcium silicate with the $Ca(OH)_2$ released during hydration of cement and increases strength. Like silica and glass powder, silica fume has a definite cesium sorption capacity due to the formation of surface hydroxyl groups. Precipitated silica and glass powder are, however, more cost effective than silica fume.

2.8.1.4. Other minerals

The presence of sulphide ores in natural reactor zones at Gabon and in uranium deposits at Cigar Lake area indicate that the leaching of fission products has taken place under reducing conditions. The minerals found in these regions are of interest as admixtures to CWP and backfills intended for near surface disposal facilities to immobilize radionuclides. The minerals of interest are apatite, calcite, galena and illite, the latter being a degradation product of bentonite.

2.8.2. Organic admixtures

2.8.2.1. Super plasticizers

Superplasticisers are used in cement concretes to reduce the water to cement ratio by imparting fluidity. Naphthalene β sulphonates and its polymer with formaldehyde are common superplasticisers. They enable lower water to cement ratios and ensure higher strength, lower porosity and permeability of CWP. Porosity and permeability of CWP are directly related to diffusion and leaching characteristics of incorporated radionuclides. Their effectiveness is dependent on CWP composition.

2.8.2.2. Monomers and polymers

Organic liquid admixtures like methyl cellulose, polyacrylamide, unsaturated polyester resins, and styrene and polymer powders can be dispersed in the aqueous phase. The presence of polymers, like superplasticisers, results in decreased porosity and enhanced workability. In situ polymerization during setting of CWP reduces its porosity. However the peroxide type accelerators tend to decompose in alkaline media of LLW sludges and ILW. Activated carbons or carbon fibres having high free electrons/radicals on their surface may be used as admixture to accelerate the polymerization.

2.9. SUMMARY

The nuclear industry generates a wide variety of potentially soluble or mobile wastes which require solidification. The wastes differ from country to country, depending on the size and scope of the nuclear programme. For example, reprocessing tends to generate chemical wastes containing tributyl phosphate and salt – rich wastes whereas pond storage of 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 pre-treatment 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. While these give short term improvement the long term fate of these materials in cement is less certain.

3. NOVEL MATERIALS

Some concern has been expressed about the limitations of conventional cement systems, for example their high pH and intolerance to certain process chemicals present in waste streams. Thus considerable interest exists in using cementitious materials with lower pH of pore water, perhaps even extending it into acid regimes, pH<7. Additionally, alternative formulations may improve the matrix binding capacity for selected radionuclides and may also reduce the set retardation caused by inactive components, e.g. zinc salts, borates. The CRP has discussed progress achieved so far on four types of alternative cementitious systems as shown in Table 12.

TABLE 12. REPRESENTATIVE NON-PORTLAND CEMENT SYSTEMS

Designation	Formation conditions	Comments
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 (MKP)	Many variants are known, differing in pH and solubility. Not fully commercial except for small scale applications, e.g. as refractory or dental cements
Calcium sulfoaluminate cement (CSA or C$A, where $=$SO_3$)	Available commercially or made by mixing commercial calcium aluminate cement (CAC) with calcium sulfate	Has a history of use (~40 years) as a construction cement. Developed in China but now widely available.
Calcium aluminate cement (CAC)	Based on clinkers or fused products with dicalcium silicate and $CaAl_2O_4$	Calcium aluminate cements are widely available as commercial products with a long history of use in construction.

The most engineering experience has been achieved with CAC and C$A cements. Both types handle and mix like Portland cement and are physically compatible with hardened OPC, to which they bond strongly. Both CAC and C$A cement can be used with fine mineral aggregates to make free flowing gouts or mortars, or with aggregate to make concrete. Both types set and gain strength more rapidly than PC. Indeed C$A is often sold with a retarder incorporated to ensure a period of workability. On the other hand, both CAC and C$A compositions have relatively high heat of hydration which is liberated over a shorter period of time than comparable Portland cement mixes. The heat evolution in large size monoliths may have to be managed to avoid thermal cracking.

There are, however, important differences between the two types. CAC cement is sulfate free and hardens to give mainly hydrated calcium aluminates or carboaluminates with C-S-H: $Ca(OH)_2$ is absent. Some of the matrix forming hydrates become unstable in warm conditions and on that account, CAC cements may lose strength in service above 20ºC in moist environments. The sequence of phase changes in the hydrate phase assemblage is termed "conversion". On that account, CAC cements should be used with caution where thermal excursions or prolonged warm service is anticipated. On the other hand, C$A cements avoid this problem: the hardened paste of C$A cement contains a high proportion of ettringite, a hydrated calcium sulfoaluminate, AFt, together with smaller amounts of AFm and C-S-H. Calcium hydroxide is again absent.

In both CAC and C$A types, the absence of portlandite, $Ca(OH)_2$, amongst the hydration products gives rise to a matrix with an internal pH about 1 unit less than of comparable Portland cement matrices. Nevertheless, both types have sufficiently high pH, c. 11.5, to give adequate corrosion protection for embedded steel as well as good pH buffering capacity, so the pH is well maintained in service environments.

The water demand for hydration of C$A compositions is characteristically greater than that required for fluidity, particularly if a superplasticiser is included, with the result that it is possible to have a "dry" internal environment. In this context "dry" means that that liquid water is absent. This dry environment is especially favourable to slow reaction between cement and embedded electropositive metals such as Magnox, with the result that hydrogen evolution ceases to be a problem.

Although C$A cements have a shorter history of use than Portland, it is apparent from older (c. 30 year) constructions that no major durability problems have been encountered. CAC cements have recently celebrated their first century of commercial use in engineered structures. Both CAC and C$A cements, although alkaline, exhibit moderate resistance to acid attack. Moreover both types, C$A and CAC, have excellent resistance to attack by sulfate and chloride containing ground waters. Both types are amenable to chemical manipulation by means of additives and, on that account, are often used in special applications for example in self-levelling floor screeds, tile setting cements and as repair materials for Portland cement. It is difficult to compare leach resistance values directly but, as reported here, the permeability and leachability of C$A cements is satisfactory to excellent.

The geopolymer type materials such as SIAL are made from alkali silicate (sodium, potassium) and metakaolin. This type of cement is both new and old: old in the sense that it has a history of patenting and small scale application extending over more than a century but novel inasmuch as it has only recently been considered for use in structural and large scale applications. Basically the reactants are kaolin, a naturally occurring clay mineral, calcined at ~ 700–750 ºC so as to expel structural water but at low enough temperature partially to preserve the basic layer structure of the precursor mineral. The resulting powder is mixed with a concentrated aqueous solution of alkali silicate; the sodium silicate is sold as "water glass". Waste is added at the fluid stage. Setting and hardening follow. Hardening is frequently accelerated by liberated heat or using warm, c. 40ºC, curing. The favourable experiences reported here suggest that more widespread applications to waste conditioning are possible. Nevertheless we lack standards for the precursors and experience of process optimization. Also, and perhaps crucially, the long term stability of these materials has not been demonstrated. The binding phase appears to be an amorphous but rigid alkali aluminosilicate gel about which little is known. However research activity in non-nuclear applications of geopolymers is active and is likely to generate more knowledge of formulation and in particular, their long term durability. These confidence building exercises will influence the application potential for geopolymers in the nuclear field.

Phosphate cements also receive attention for radioactive waste conditioning. These cements are long known but have had mainly niche applications, e.g. zinc phosphate cements in dentistry. Most of the experience in the nuclear field is with magnesium potassium phosphate (MPP) cements. These consist of dead burned MgO plus a source of soluble phosphate, for example monopotassium phosphate (MKP). The reaction between the MgO and acid phosphate is an acid base reaction which, in the presence of water, results in precipitation of magnesium potassium phosphate salts. For example when MgO and magnesium potassium phosphate (MKP) are mixed with H_2O in the proportions 1:1: 5 moles, respectively, the resulting reaction product is struvite, $MgKPO_4 \cdot 6H_2O$, a crystalline material that forms a dense cementitious ceramic (often termed a "cold ceramic").

$$MgO + KH_2PO_4 + 5H_2O \rightarrow MgKPO_46H_2O$$

Thus these phosphate cements bridge a gap between conventional ceramics and Portland cements. For this system, a cure temperature between 60° to 65° C is required to produce a monolithic product. At lower temperatures, the reaction to struvite, $MgKPO_4 \cdot 6H_2O$, is incomplete and the resulting reaction products are amorphous hydrated phosphate phase(s) which are less dense and not durable.

The reactivity of MPP cement is controlled by the reactivity of the MgO which, in turn, is a function of its calcinination temperature and particle size. (The higher the temperature, the harder the product is to grind, i.e. larger particles and the slower the reaction rate). Set retarders such as boric acid are also used to achieve the desired working time. MPP cements do not have classical induction (dormant) periods typical of Portland cements: the use of set retarders can extend the final set for days to weeks at a more or less constant rate. This feature allows for balancing the heat production and dissipation rates.

These materials handle and mix like Portland cements and have been successfully formulated at full (200L) scale. In packaged magnesium potassium phosphate products based on MgO and MKP, the stoichiometric ratio is often not used because a portion of the dead / hard burned MgO is not reactive. Consequently, the amount of MKP is reportedly reduced by up to 30 weight percent to eliminate potassium and phosphate leaching which causes an increase in porosity and efflorescence. However the rheology of MPP waste forms and backfills is less sensitive to the amount of water in the mix and to temperature than that of Portland cements. Compressive strength is more sensitive to the amount of MPP in the mixture. Inert aggregates (powders, sand, and gravel) can be used to reduce the heat generation and modify/enhance the rheology.

Magnesium potassium phosphate cements typically exhibit a slight expansion, 1 to 2 volume percent (measured on pastes: less for mortars and concrete), when prepared in stoichiometric proportions for commercial applications. Consequently, excellent bonding to substrates, including stainless steel and aluminium metal, is a characteristic of these materials.

Magnesium potassium phosphate based cements have limited use in the construction industry for a variety of structural applications including rapid set road and runway repairs and rock anchor bolt cements. Thus they have some track record of persistence in the natural environment.

Conclusions

Limitations in the properties of Portland cement have led to the development of novel binders. Many types of novel cement have been reported but the four selected for discussion here are additionally described in individual reports, together with application examples. An example is the stabilization of soluble zinc salts: they interfere with hydration of Portland cement but are well tolerated in C$A cements. Some novel cements have a history of commercial use and are known to be durable in a range of natural service environments. Standards are also available for C$A and CAC cements. Although used the geopolymer and phosphate type cements still require optimization with promising research results reported here. For novel and conventional cementitious materials emplaced in the same repository no incompatibility problems have been identified.

4. TESTING OF CEMENTITIOUS MATERIALS

Safe management of radioactive waste requires a system consisting of waste packages, containers, backfills, engineered and natural barriers that all contributes together to the safety of a waste repository. The durability of cementitious materials is an important issue and their proper characterization using various methods plays a major role in the understanding of the use of such material for storage, transportation and disposal. The durability of cementitious materials based on the designed specifications, can only be quantified over long periods of research. However, due to time constrains, short term characteristics such as the compression strength, tensile strength, porosity, sorptivity, and permeability (leaching) are determined to be used in models aiming to determine the possible durability of these cementitious material that satisfy waste acceptance standards. Examples of short term characterization techniques used during this CRP are summarized in Table 13. These comprise both well-known standards (see Strategy and Methodology for Radioactive Waste Characterization. IAEA-TECDOC-1537, IAEA, Vienna (2007)) and novel techniques.

TABLE 13. EXAMPLES OF TECHNIQUES USED WITHIN CRP FOR TESTING OF CEMENTITIOUS MATERIALS

Property	Characterization tests
Composition	BET, DTA, XRD
Porosity	ASTM D 4284, Gravimetrical methods, Neutron imaging, Mercury Intrusion Porosimetry (MIP)
Leaching	ISO method, ANSI/ANS-16.1-1986, Czech Nuclear Authority (SUJB) number 32811/2007.
Sorptivity	Neutron imaging
Hydraulic conductivity & Permeability,	Permeability Test (ASTM D 5084)
Pore size distribution	Neutron imaging, MIP
Thermal cycles	European standard EN 196-9
Micro structure and chemical composition	SEM, EDX, STEM, Neutron imaging, Acoustic emission, FTIR
Gas permeability	Torrent methods (ASTM C 577)
Specific gravity	ASTM C 642
Compressive strength	KS L 5105 (Korean standard), TEST N.278 (Slovakia)
Bulk density	KS F 2308 (Korean standard)
Biodegradability	Ukrainian requirements (NP 306. 608-95), GOST (Russian Federation)

Most participants of CRP have used standard well-known methods for determining characteristics of cementitous materials in order to be used for durability calculations [Table 13]. Alternative characterization techniques for cementitious materials, such as neutron imaging, acoustic emission, STEM and FTIR were demonstrated as possible techniques to complement the study of the durability of cementitious materials (see Table 13). The additional techniques could be useful for design parameters in geotechnical and structural engineering. Short descriptions of these techniques are given below.

4.1. NEUTRON IMAGING

The porosity and sorptivity tests may be defined as techniques that measure the early age resistance of concrete to the transport of fluids through it. The purpose of the neutron imaging tests is not to determine absolute or intrinsic material characteristics, but to produce reliable values to be used for comparative purposes. Neutron radiography (NRad) is a useful, non-destructive method for determining hydrogen content in various materials. Hydrogen content in samples is determined by quantitative analysis of measured profiles of neutron attenuation in the samples. Thermal neutrons are attenuated (mostly scattered) to a significant degree by hydrogen, and substances that contain hydrogen. Thus, neutron images of porous media containing water can provide an accurate indication of the pore structure of the media.

Neutron radiography is a non-destructive examination (NDE) technique based on imaging using penetrating neutron radiation to produce 2-D images, called radiographs, on samples under investigation. Being a non-destructive analytical tool, radiography enables the visualization of interior features of objects without physical modification of the object under investigation. The industrial system requires linear geometry setup of the radiation source, sample stage and detection system. When neutrons pass through an object they can be scattered, absorbed and transmitted.

The transmitted component of the interaction is detected using radiography and provides information about materials that constitute the object under investigation according to the Beer-Lambert law:

$$I = I_0 e^{-\Sigma d}$$

where I_0 and I are the intensities of the beam before and after passing through the sample respectively, and Σ and d are the linear attenuation coefficient (cm^{-1}) and the thickness (cm) of the sample respectively. The linear attenuation coefficient is a function of the atomic number and neutron energy which enables radiography to visualize material of different atomic numbers.

Neutron tomography is a 3-D non-destructive examination (NDE) technique based on reconstruction of a virtual 3-D image of the object under investigation using 2-D images obtained at different angles of rotation of the object under investigation for angles at least 180°. The thermal neutron imaging facility at the SAFARI-1 reactor was used to map the water transport through the cement applying radiography and tomography as analytical tools. At 20 MW reactor power and using a 21 mm interior pinhole diameter neutron passage in the collimator, a 93% thermal neutron flux of 1.2 10^7 n cm^{-2} s^{-1} is delivered at the object position in the centre of the beam. Images are captured via a lithium based zinc sulphate scintillator screen using a Peltier cooled Charged Coupled Device (CCD) camera with a 1024 x 1024 pixel array and 16-bit image output device. The system has a 2 µs/image readout capability. Using a 100 mm x 100 mm field of view (FOV), a resolution of 0.098 mm/pixel size is achieved. This means that 2-D images (NR) have a 0.0096 mm^2, and 3-D images (NCT) a

0.0009 mm^3, spatial resolution limitation respectively at the 1 horizontal binning and 1 vertical binning of pixels. Binning of pixels horizontally and vertically on the CCD is the concept of grouping a number of pixels into one pixel, thereby affecting the intensity and the spatial resolution.

4.2. WATER SORPTIVITY MEASUREMENTS

For sorptivity measurements by neutron radiography dried waste form specimens samples were tightly enclosed in aluminium tape with only the circular bottom faces of the samples exposed, facilitating water transport in one direction only (upwards). The exposed base of each sample was continuously immersed in water to a depth of approximately 2 mm and adsorption measured over periods of 1, 2, 4, 6, 9, 12, 16, 20 and 25 minutes, and for longer time periods (up to a month) where possible. At the end of each time interval the samples were removed from the water, weighed and then transferred to the NR facility to collect 2-D radiographic data and chart water ingress. A rig was specially designed for the radiography facility so that the uncovered face of the samples remained immersed during data acquisition. The 2-D images were obtained over a 3 second exposure time each with horizontal and vertical pixel binning settings of 4 and 1 respectively, resulting in spatial resolution limits of 0.391 mm/pixel and 0.098 mm/pixel respectively. The water could be visualized within each sample after each water absorption period, and a thick line profile was used to obtain intensity data from the sample image (Fig. 8(a)). From the curve of intensity as a function of the length of the sample, the water front could be determined as shown by dotted marker on Fig. 8(b).

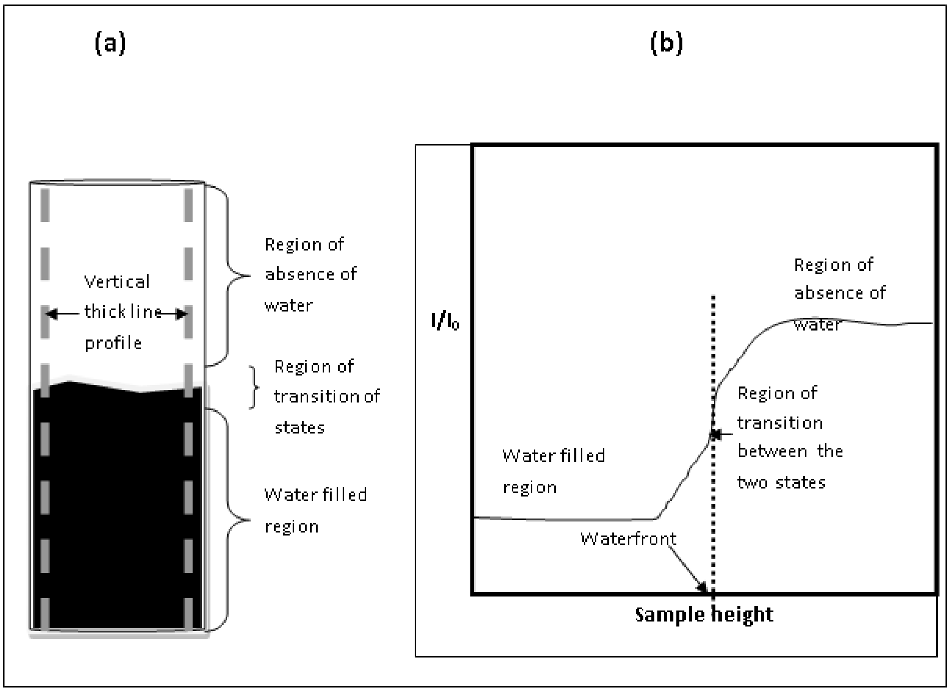


FIG. 8. (a) Schematic diagram of a radiograph showing a water front within a cylindrical mortar sample and (b) Determination of the water front height from the resulting curve of intensity as a function of sample height.

4.3. MACRO PORE DISTRIBUTION DETERMINATION

The 3-D neutron tomography investigation was performed on completely dried specimens to determine macro-pore distributions (see Appendix, Australia). These 3-D images were obtained from the reconstruction of 360 x 2-D images acquired over a 20 second exposure period for each of the 2-D images. A 3-D image (tomogram) is composed of slice images. The slice images are reconstructed from a series of radiographs (projections) taken at different angles of rotation of the sample. The reconstruction of slice images was performed using OCTOPUS software and the analysis of 3-D image was carried out using VGStudio Max visualization software.

OCTOPUS reconstructs cross-sectional images (slices) of the sample using a filter back projection reconstruction algorithm. Image correction (background, electronic, beam hardening and beam fluctuation corrections) is carried out before the reconstruction. The result of reconstruction is a stack of slice images numbered according to their position on the sample from top to bottom, as depicted in Fig. 9(a). VGStudio Max visualization software provides a 3-D visualization and analysis of the stack of slice images. The stack is analysed as a 3-D image representation of the sample. Each region of the volume is represented by voxels (volume elements). The defect detection tool of VGStudio was used to detect pores and to provide their size and location inside the volume of the sample, as shown in Fig. 9(b).

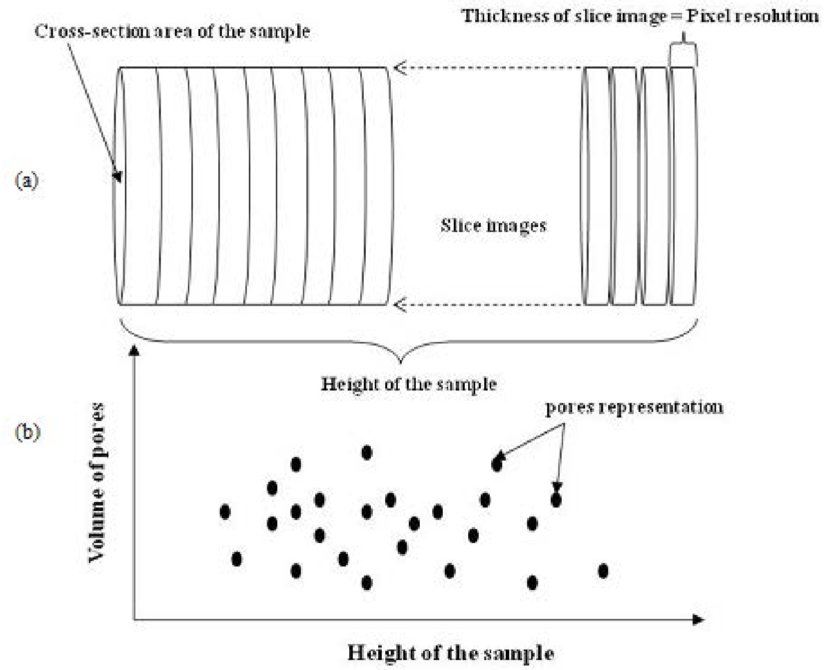


FIG. 9. (a) Schematic diagram showing the constitution of sample height from slice images and (b) presentation of pore size distribution as a function of sample height

VGStudio Max visualization software provides a 3-D visualization and analysis of the stack of slice images. The stack is analyzed as a 3-D image representation of the sample. Each region of the volume is represented by voxels (volume elements). The defect detection tool of VGStudio was used to detect pores and to provide their size and location inside the volume of the sample, as shown in Fig. 9. The minimum pore volume that can be detected is a voxel resolution and is equal to the product of x, y and z where x, y and z are the dimensional size of the voxel.

4.4. POROSITY MEASUREMENTS

Preparation of the sample for the porosity test was the same as for the NRad sorptivity tests. The samples were initially dried in an oven, measured and weighed to obtain their density and then subjected to a vacuum for 1 h to ensure that all the air was removed. After this treatment a neutron radiography image was captured (I_{Dry}). After this initial image of the dry waste forms were captured, the waste forms were subjected to a vacuum for 1 h to ensure that all the air was removed and then saturated with water under the vacuum for another hour. The saturated waste forms were removed and put into the neutron beam at exactly the same geometry as before to capture the saturated neutron image (I_{Sat}). Porosity was calculated using the equation:

$$Porosity = \frac{ln(\frac{I_{Sat}}{I_{Dry}})}{h\rho_w\mu_w}$$

where h is the thickness of the specimen in cm, μ_w is the thermal neutron attenuation of water obtained for the specific specimen geometry in cm^2/g and ρ_w is the density of water in g/cm^3.

4.5. ACOUSTIC EMISSION

In general, acoustic emission (AE) is defined as elastic waves originating in consequence of local, dynamic and irreversible changes in the material structure. A typical AE system consists of signal detection, amplification, data acquisition, processing and analysis. Various parameters are used in AE to identify the nature of the source, including: count, duration, amplitude, rise time, energy, frequency and RMS (Root Mean Square) as indicated in Fig. 10. The technique involves applying a load to a solid structure (e.g. by internal pressure or by external mechanical means) until it begins to deform elastically. Associated with this elastic deformation are changes in the structure's stress distribution and storage of elastic strain energy AE is a natural occurring phenomenon associated with sudden release of elastic energy propagating in the form of transient waves caused by mechanical deformation, dislocation movement, phase transformation or other irreversible mechanical changes within different materials. The largest scale AE sources are the seismic events whereas processes that still generate detectible AE are microscopic defect movements of the order of a few pycnometers in a stressed structure. The collection and processing of AE waves was developed and established as a non-destructive testing and evaluation (NDT&E) method particularly shown as a powerful tool for characterization of failure mechanisms and damage assessment in various materials and structures.

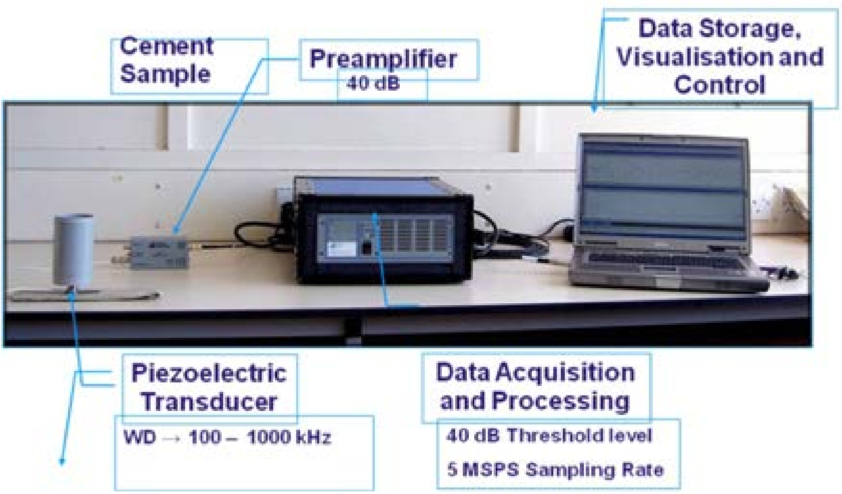


FIG. 10. Acoustic emission technique used in current CRP.

The AE technique offers several advantages which make it a potentially suitable tool for non-destructive testing and inspection of nuclear waste packages. These are related to the high sensitivity of the method to micro and macro mechanical events within the structures providing an early indication for the damage development in situ, the possibility to be used as a passive testing method without additional stimuli to be applied and, in theory, unlimited duration of monitoring. As the load increases further, some permanent microscopic deformation may occur, which is accompanied by a release of stored energy, partly in the form of propagating elastic waves termed 'Acoustic Emission' (AE). If these emissions are above a certain threshold level they can be detected and converted to voltage signals by sensitive piezoelectric transducers mounted on the structure's surface. AE is a natural occurring phenomenon associated with sudden release of elastic energy propagating in the form of transient waves caused by mechanical deformation. The largest scale AE sources are the seismic events whereas processes that still generate detectible AE are microscopic defect movements of the order of a few pycnometers in a stressed structure. The collection and processing of AE waves was developed and established as a non-destructive testing and evaluation (NDT&E) method particularly shown as a powerful tool for characterization of failure mechanisms and damage assessment in various materials and structures.

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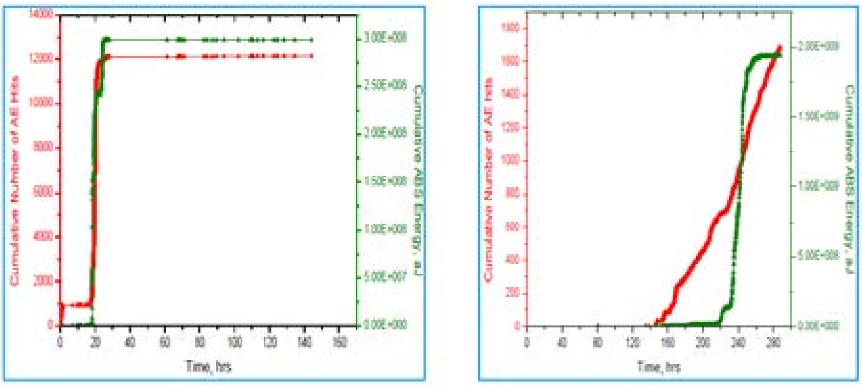
An AE technique was used during this CRP for early detection, characterization and time progress description of cracking phenomenon caused by the corrosion of Al encapsulated in cement matrix (see Appendix, United Kingdom, Sheffield University). The study was conducted on an ordinary Portland cement (OPC) system encapsulating high purity Al metal. The AE experimental setup consists of a piezoelectric AE transducer (or sensor) with a diameter of 17 mm was attached to the bottom of the container with the cement based sample via a thin layer of grease for acoustic coupling. Although the quality of the sensor coupling affects the reproducibility of the characteristics of the detected AE waves all experiments on the cementitious samples were conducted by the same operator following the same procedure minimizing random effects. A wideband transducer, type WD, calibrated and supplied by Physical Acoustics Corporation (PAC) has been chosen due to its high sensitivity in a broad range of frequencies between 100 and 1000 kHz. The electrical signals (voltage) generated by the AE transducer were amplified by 40 dB and passed through a band pass filter between 20 kHz and 3 MHz. Then each of the analogue signals was measured, and if above the threshold level of 40 dB [25], was sampled and quantized by 18 bits analogue to digital converter (ADC) with 5 MSPS sampling rate. A hit driven data acquisition process with PCI-2 based AE system, supplied and calibrated by PAC, was used. When an AE wave was detected from the transducer attached to the sample, the generated electrical signal amplified by a preamplifier type 2/4/6 from PAC and its amplitude exceeded the threshold level data streaming was allowed. The data recorded on a PC hard drive in an ASCII file for each AE signal (or hit) consisted of a set of parameters such as duration, amplitude, counts, rise time and absolute (ABS) energy. The waveform of each filtered and recorded AE signal was stored in the PC memory. The pre-trigger time (in µs) used to record the signal waveform before the first threshold level crossing was set at 100 µs. Selective cross-plots such as hits amplitude versus duration and histograms plotted by PAC AEwin software package provided real time information for the AE from the sample under monitoring.

A large number of 2328 AE hits were recorded from the BFS/OPC sample with encapsulated Al for 183.5 hours of monitoring separated into clearly defined periods with very low or almost none activity followed by an abrupt jump in the AE hits number. This behaviour of the sample, in term of AE, resembled the response of studied cement based structures under loading associated with micro and macro scale damage development. The result in Fig. 11 is an example of monitoring the performance of cement based materials encapsulating metallic wastes such as aluminium with this technique.



Signal after mixing OPC + Al   Signal after 90 day of OPC and Al

FIG. 11. Cumulative number of AE hits and associated ABS energy detected during the AE monitoring of the BFS/OPC samples with encapsulated Al.

Despite of some differences found in the AE hits rate and their time distribution detected from the BFS/OPC sample with encapsulated Al in comparison with those from the reference OPC structure under identical experimental conditions, the AE signals detected have been successfully classified based on similar parameters and frequency characteristics. To evaluate the feasibility of the method for industrial use an optimization of the experimental setup will be required as well as additional research to assess the importance of various parameters such as sensor frequency characteristics, positioning and coupling, background noise, waste type and loading, container volume and shape.

4.6. STEM

The microstructure and chemical composition of the cement pastes can be investigated using SEM while X ray microanalyses can be performed using an energy dispersive X ray system (EDX EDAX type). Hydrated cement samples can be prepared for STEM-in-SEM or TEM analysis by dispersing in material in methanol using an ultrasonic bath. The dispersion is repeated to obtain a very low material concentration.

In the STEM-in-SEM mode (FEI ESEM XL-30), analyses are done by placing a drop of suspension (sample) onto a 3 mm diameter TEM 200 mesh copper grid covered on the back with a holey carbon film on the head of a TEM sample holder fixed on a vertical axis. As the incident electron beam passes through the sample a signal is collected by an annular semiconductor detector (used for the collection of backscattered electrons), placed below the sample. The detector collects scattered electrons generated by the sample, while transmitted electrons passing through the hole at the centre of the STEM detector. Using this type of setup, a larger amount of the scattered electrons could be collected on the detector. This results in the formation of an image as well as high contrast dark field images. The much lower electron energy (30 kV) used for the STEM-in-SEM analysis has two main advantages over using TEM analysis. The first is that the degradation of fragile phases such as ettringite under the electron beam during analysis is limited. Secondly, as the contrast enhancement is improved, a reduced excitation volume is required resulting in an increase in electron scattering cross-section for analysis. An example of a STEM-in-SEM/EDX microanalysis of ettringite analysed in cement paste during this CRP using this technique can be seen in Fig. 12.

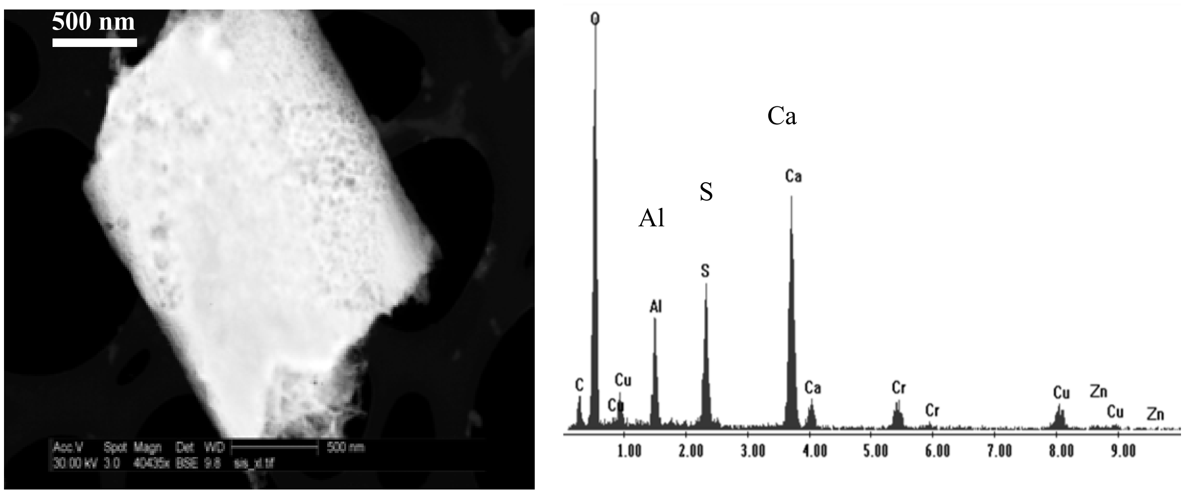


FIG. 12. STEM-in-SEM/EDX microanalysis of ettringite (carbon comes from the sample holder, Cu from the copper grid, and Cr from the detector).

Additional observations can be made using a 200 kV field emission gun Transmission Electron Microscope (JEOL 2010F) equipped with an energy dispersive spectrometry system (INCA-OXFORD EDX) with a detector dedicated to light element detection.

4.7. FTIR

Infrared spectroscopy is a known analysis technique for identifying compounds by measuring the interaction between light and vibrational motion of the covalent chemical bonds in molecules and in the covalent bonds in lattice ionic crystals. The system consist of an infrared source, a device to decode the radiation into frequency and intensity information, a pathway for this encoded radiation to interact with the sample and a detector recorder. A plot of measured infrared light versus wave number provides a unique infrared spectrum as for a specific infrared active compound that follows Beer-Lambert law as mentioned previously ($A = \varepsilon.c.L$). However, the application of this technology to the structure of cementitous waste for instance a SIAL® matrix is possibly a new application of this technology. This can be done by pulverizing approximately 3.0 mg of SIAL® matrix together with 200 mg of dry KBr powder, before pressing mixture at 100 MPa into a pellet. An example of an infrared spectrum of a SIAL® matrix recorded by a standard FTIR instrument is presented in Fig. 13.

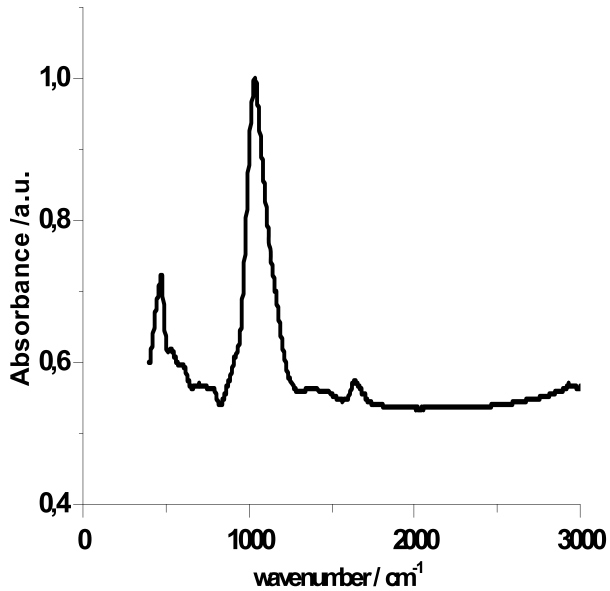


FIG. 13. Infrared spectra of SIAL® matrix sample.

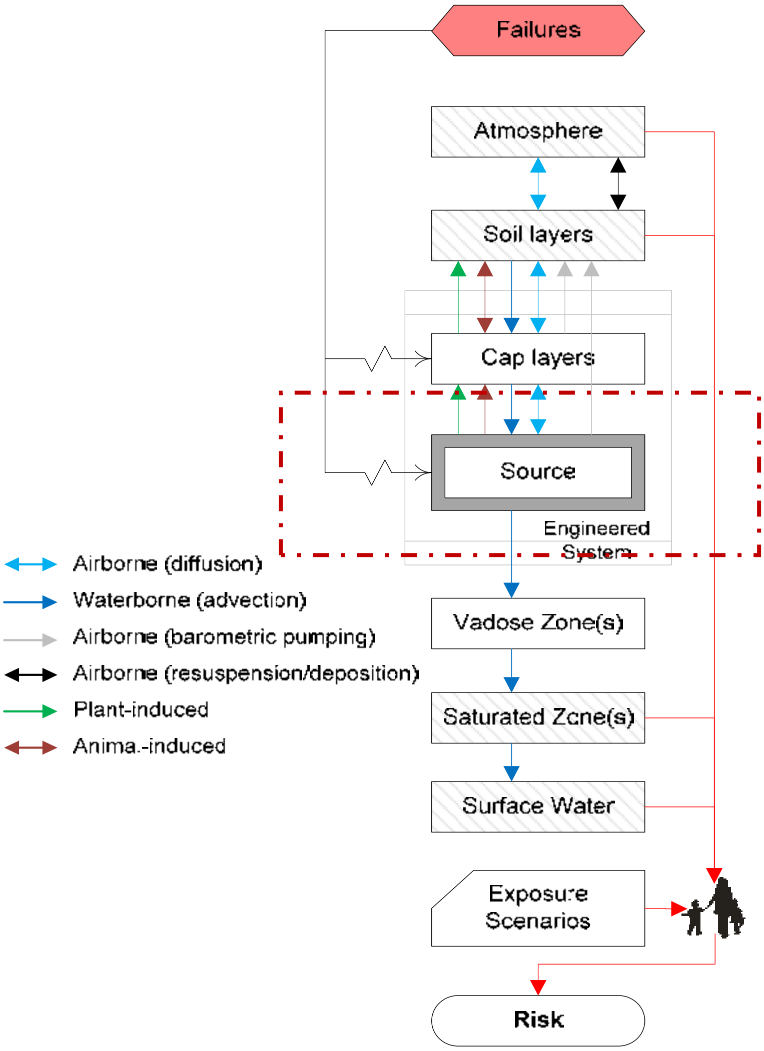
The result in Fig. 14 indicated a absorption spectra for aluminosilicate (consisting of superposed Si-O$^-$ and Al–O$^-$ stretching vibration) between 800 cm^{-1} and 1200 cm^{-1}. As this vibrational frequency corresponds to both amorphous and crystalline phase in aluminosilicate, it is difficult to differentiate and determine the ratio between amorphous glassy phase and crystalline phase and other additional techniques such as X ray diffraction should be utilized to determine amorphous character of the SIAL® matrix.

Conclusion

The durability of cementitious materials is an important issue and the measuring thereof plays a major part in the understanding of the use of such material. Short term characterization results can only be used as a guideline for waste form development and durability predictions.

5. MODELLING

Performance of cementitious barriers used for radionuclide applications, e.g. radioactive waste forms, containment structures, and back fills, can be assessed depending on application and its time span. The first level involves characterization and testing to demonstrate compliance with the requirements and suitability for shallow land (near surface) applications. Satisfying these requirements is intended to demonstrate that a cementitious barrier (typically a waste form) is a non-dispersible solid that can meet minimum leaching standards for exposure to water or a corrosive solution. Additional analyses are required to address performance under site specific conditions and as a function of time because cementitious barriers may be expected to perform one or more physicochemical functions needed for waste / contaminant isolation over time frames of hundreds, thousands or possibly tens of thousands of years. Hence the concept of durability i.e., performance of design function for design life time (service life), is introduced as an additional measure of performance.



Cementitious wasteforms (PA source terms) and cementitious barriers (containers and containment structures) are part of engineered systems. Durability over time and changing conditions of these cementitious barriers are necessary inputs to disposal facility performance assessments.

Characterization of the interfacial regions and conditions between the cementitious barriers and the environment are important to provide near-field source terms for radionuclides.

Uncertainty analyses of the durability of the cementitious barriers in the disposal facility are broadly applicable to the performance assessment process.

FIG. 14. Relationship between durability analysis of engineered cementitious barriers (limited to processes and features for engineered materials indicated by red dashed line) and disposal facility overall performance assessment (dose analysis).

Cementitious barriers used for low level waste (LLW) and intermediate level waste (ILW) may be expected to perform one or more of the following functions over a range of time frames depending on the half-lives of the radionuclides in the material and also in the disposal facility:

— Waste conditioning and contaminant stabilization (physical and chemical stabilization);
— Physical containment to isolate the contaminated waste from the environment;
— Physical barrier to reduce water infiltration;
— Intruder protection.

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 and in some cases the need for durability evaluations is not recognized. Strategies and methods used to quantify and predict the performance of modern high quality civil/commercial structures for 100 to

120 years are applicable to LLW cementitious barriers. However, the performance periods for cementitious materials used in radioactive waste disposal scenarios are expected to perform for longer times than are expected for civil structures, i.e., 300 to 500 years and to barriers for long lived mobile isotopes for ILW which have longer performance requirements, 1000 + years.

The durability of cementitious barriers can be assessed empirically by extrapolating short term data. This approach offers limited opportunities for mechanistic analyses of processes that occur at different rates and sensitivity analyses of one-off conditions.

Durability can also be assessed by reactive transport modelling for which parameters such as diffusivity and permeability (hydraulic conductivity) must be provided. This approach provides a mechanistic basis for durability and allows for analyses of interrelated and concurrent processes which can occur at different rates (fast processes addressed by the empirical approach and slow processes that may be relevant for the time frames required for LLW and especially ILW disposal facility performance).

Reactive transport modelling can also support sensitivity analyses (one-off) and more rigorous uncertainty analyses applied to the overall disposal facility performance assessment or safety case evaluation. In addition, this type of modelling is suited for extrapolation and prediction of changes in physical and chemical properties of engineered cementitious materials (including waste forms) as a function of changing conditions over long times.

Modelling durability has several aspects. Both conceptual models and mathematical expressions which represent the important processes that control performance (specifically flow and reactive transport models) are useful tools for analysing the level of understanding of the overall performance and for extrapolating performance beyond times for which observations and test data are available. Some of the important processes which control cementitious barrier performance include:

- Ageing;
- Exposure to leachate;
- Exposure to corrosive chemicals, such as sulphate, carbonate, alkalis, chloride, magnesium, and organic acids, which react with the matrix and degrade physical integrity;
- Structural stresses.

Parameters used to represent these processes should accurately represent the terms in the specific equations developed to describe the physical–chemical reactions. Experimental results for laboratory and field conditions are vital data sources for validating the performance models. In addition, data collected from actual cementitious barriers exposed to actual environmental conditions require interpretation but are very useful for refining the performance models and predicting service life.

Moisture and gas movement through porous solids is represented by both advective and diffusive terms. The following physical / hydraulic properties are needed to model this type of transport: bulk and transmissive porosity, permeability and hydraulic conductivity, bulk and particle density, water diffusivity, ionic diffusivity and tortuosity. In the case of fractured cementitious material, two phase flow should be considered because the material itself is inherently porous (micro pores) with transport being controlled by diffusion whereas fractures may be on a scale where transport is controlled by advection.

Parameters used to describe and model leachability are needed for both, the cementitious matrix and also to radionuclides phases. Examples of the parameters used to describe the leachability in reactive transport models include: bulk chemistry, radionuclide concentrations, quantitative mineralogy, pore solution composition, leachate chemistry as a function of pH and Eh, and leachate to sample ratio. In addition thermodynamic data and/or solubility data for the matrix phases are required. Thermodynamic data and sorption data for the phases and speciation of the radionuclides in water are also needed.

In a chemical approach to cementitious materials degradation under simple leaching conditions, four states of evolution of cements are suggested for benchmarking. These stages are achieved by sacrificial dissolution of cement substance as shown in Fig. 15 and are summarized as follows:

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: C-S-H, depending on composition, pH is buffered in the range 10 to 12.

Stage IV: Only degradation and reaction products are left to condition pH.

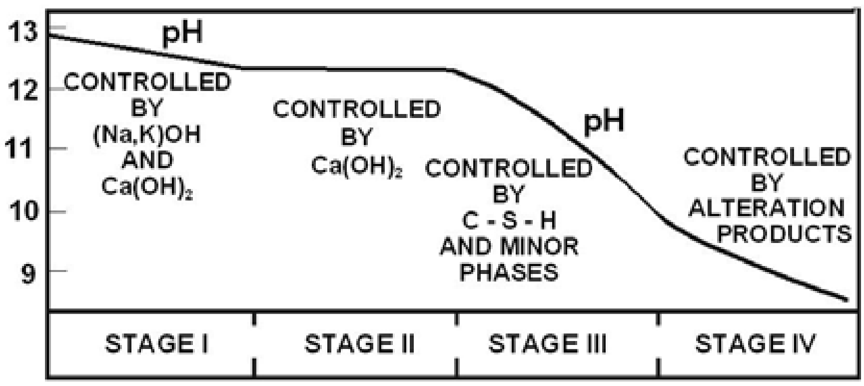


FIG. 15. Evolution of cements in a disposal environment.

The four stage approach is used in performance assessments for radioactive waste repositories for geochemical modelling of cementitious barrier durability with respect to providing chemical buffering for radionuclide phases and also physical / hydraulic durability (porosity, permeability and tortuosity) of the matrix portion of the barrier.

The objective is to estimate the lifetime of the buffer, for example how long the desirable high pH may persist, and to predict the evolution of the near field chemistry, which is needed to estimate the corrosion rate of metallic containers and waste forms. The pH conditioning action depends partly on the persistence of a metastable phase, C-S-H, and more data are needed on its persistence as it may be subject to ageing as well as sacrificial dissolution.

One dimensional geochemical modelling can be used to evaluate the performance of coupled diffusive transport. This approach is often used to evaluate chemical performance of multilayer features in encountered in disposal facilities. In the simple case, it is assumed that solute transport is by diffusion only, and assumptions are made for the geochemistry of the solid–solution system. Figure 16 illustrates the one dimension conceptual diffusion model. Two dimension conceptual model can be constructed if the intent is to evaluate the performance if cracks (fast pathway) are to be taken into account.

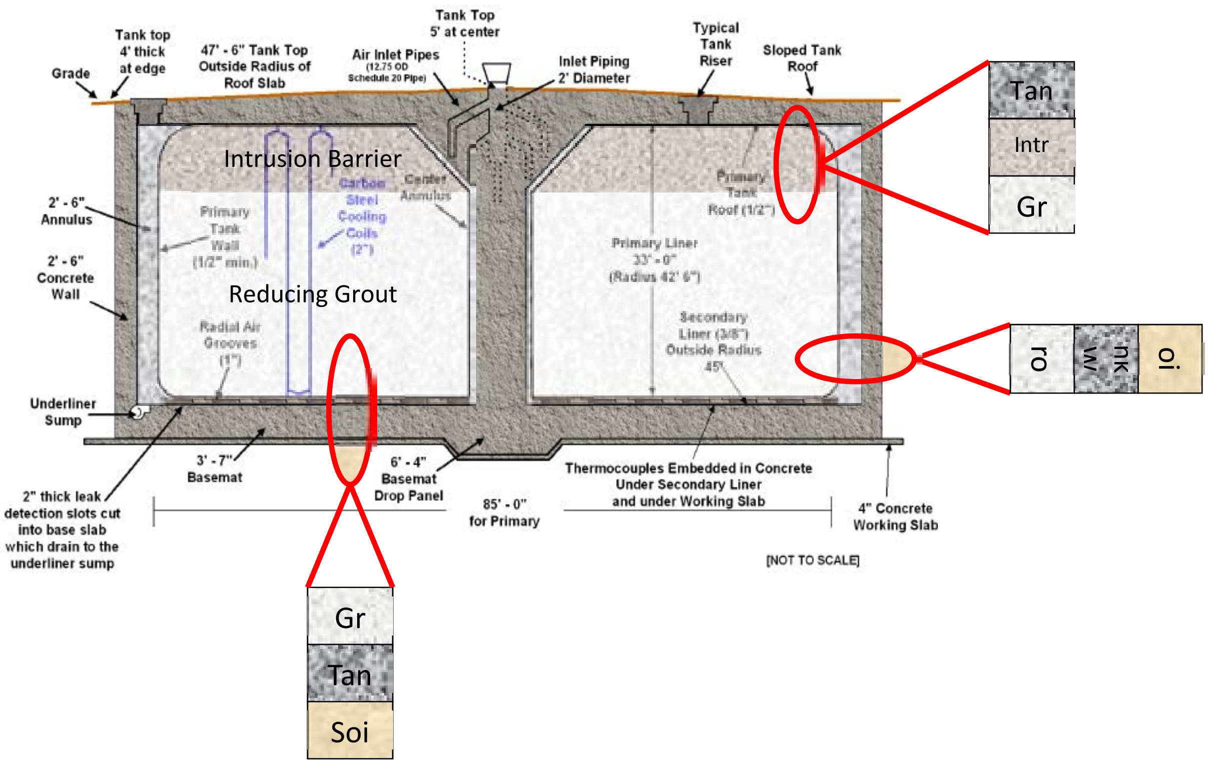


FIG 16. One dimensional conceptual model constructed to evaluate cementitious barrier performance associated with a waste tank.

The Geochemist's Workbench, PHREEQC, GEMS and ORCHESTRA are examples of computer codes used with various thermodynamic databases to predict the long term evolution of cementitious materials in the near field environment. These codes are used to link the cementitious material degradation with radionuclide sorption and solubility parameters in the near field subsurface environment.

The effect of exposure to environmental chemicals which react with the cementitious matrices is illustrated in Fig. 17. Carbonation of hydrated Portland cement results in formation of phases with the outcome of changing the porosity, pore solution composition, sorption capacity for various radionuclides, and solubility of phases containing radionuclides. These effects can be taken into account within the framework of the reactive transport models and the evolution of cementitious materials as the result of exposure to various chemical environments can be predicted over time.

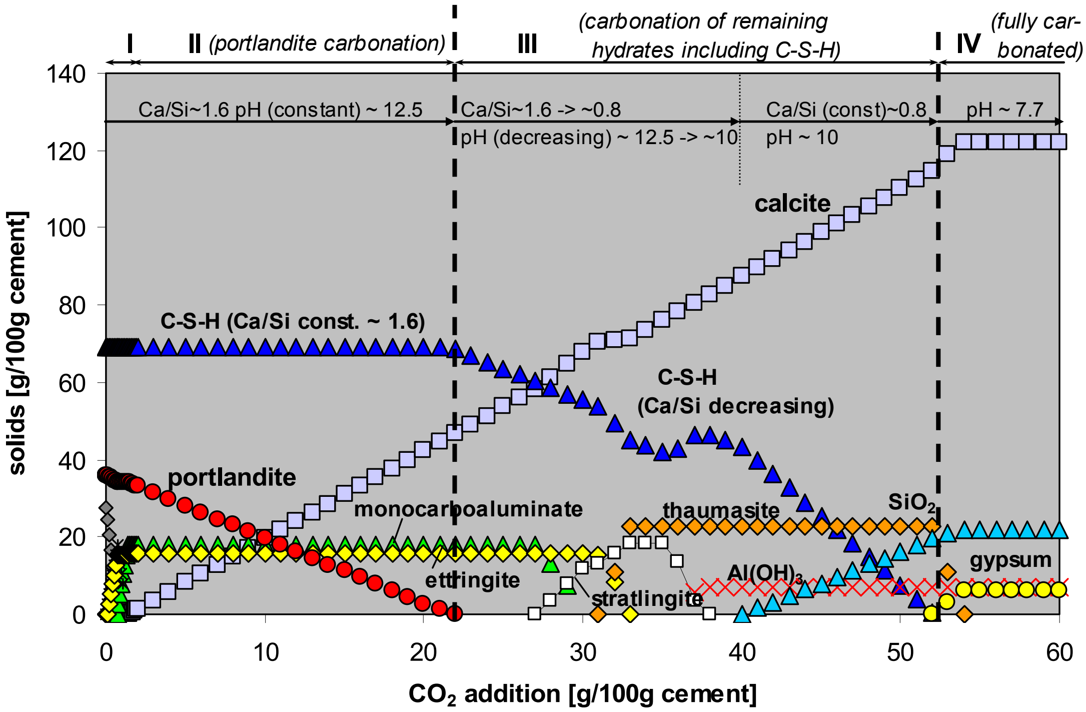


FIG. 17. Effect of carbonation on the mineralogy of hydrated ordinary Portland cement.

Increasing use of models as design and management tools has resulted in an increased emphasis on quantification of uncertainty, including significant use of sensitivity analysis to better understand the processes and design features that have the most influence on the conclusions of the assessment. Stochastic or probabilistic approaches are becoming more commonly used for sensitivity and uncertainty analysis in various aspects of performance and durability analyses.

Summary

Performance is essentially an abstract concept but can be redefined in terms of selected attributes, each of which is capable of quantification. Attributes will be chosen and weighted according to ease of quantification and anticipated functionality in the intended application. For example, permeability will be required to be high in the case of concretes intended to avoid gas pressure build up but low in barriers intended to retard a flux of radionuclide migration. Moreover each attribute does not remain constant but changes with time according to the exposure conditions in the local service environment and the deterioration of the barrier.

Figure 18 illustrates the concept. The evolution of the numerical value of a selected attribute is plotted as function of time. The user must then define the minimum (or maximum) acceptable value of the attribute, shown on the diagram as a horizontal line. When the numerical value of the selected attribute reaches this value, a construction line dropped to the time axis defines the service life.

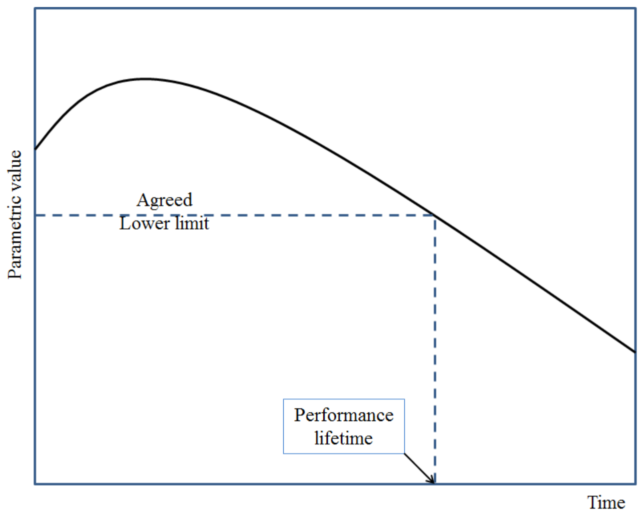


FIG. 18. Representation of durability and the relationship between parameters, time in service and performance lifetime.

The role of reactive transport models in predicting the durability of cementitious materials used for conditioning radioactive waste or as barriers for waste containment is to couple waste form and/or containment structure performance with the near field conditions and to extrapolate the evolution of these materials with time and with changing conditions. Examples of the application where reactive transport models could be useful include prediction of:

— Matrix ageing;
— Degradation to corrosive chemicals in the environment;
  - Carbonation;
  - Chloride penetration;
  - Biological degradation;
— Leaching
  - Matrix mineralogy;
  - Soluble ion chemical speciation.

Improved representation of the durability of cementitious barriers through modelling using site and material specific data can help reduce conservatism in disposal site Performance Analyses, potentially decrease near term and life cycle disposal costs, and in some cases support disposal of increased radionuclide inventories. However lack of long term performance evaluations of engineered cementitious barriers can limit (1) full utilization of disposal sites by limiting radionuclides inventories and (2) full consideration of disposal site location selection options.

6. CONCLUSIONS

The Coordinated Research Project resulted in an active interchange of experiences among leading research groups on the behaviour of cementitious materials in long term storage and disposal of radioactive waste. It has enabled to access valuable information on the underlying science and technology of cementitious materials used radioactive waste management.

Cements are a suitable material for the immobilization of a variety of waste constituents due to their favourable chemical and physical properties. The cement hydration products formed favour sorption and substitution of cationic, anionic and neutral radwaste species into cement solids while the microstructure affords physical immobilization. Cements have been extensively modified by reactive admixtures to enhance physical properties and tailor the immobilization potential for specific radwaste species or groups of species and counter the potentially harmful effect of inactive waste species.

Interactions between a cement system and the waste stream have, however, been shown to be complex, and research programmes in this area are carried out to fully understand and quantify these. Available research has highlighted that, by controlling the internal chemistry, microstructure of the matrix and the hydration products formed, through incorporation of reactive admixtures, choice of curing temperature and water /cement ratio, systems may be developed selectively to enhance immobilization of a specific waste component or group of components.

More research is required on the physical and chemical effects of waste ions on the cement structure during solidification; the formation of exotic hydration products, the speciation of waste ions and the resistance of the constituent solid phases to degradation. These interactions must be understood because apparently slight changes in matrix chemistry could result in significant change in immobilization capacity and, if this capacity is reduced, accelerate release of radioactive material into the biosphere. Waste–cement interactions, and the time dependence of the immobilization potential, are the focus of much current research.

Although numerous data are available on the release of radionuclides from various waste forms, modelling studies of the interactive processes of degradation in cementitious material is a much larger task than could be encompassed in this CRP. The local characteristics of the disposal site impose specific constraints on the evolution of barrier performance with time. Both simple and complex models are being developed: simple models as tools for semi-quantitative assessments and more complex and sophisticated models to couple processes, including reactive transport, with other chemical and physical degradation mechanisms.

To verify the durability of the waste forms, several leaching methods have been defined but none have been subject to sufficient critical scrutiny to be considered as standard. Tests are available for both static and dynamic conditions, but irrespective of the test method, analytical work is required following leach tests. Variables affecting the leaching rate during testing have to be agreed as appropriate. Defining "appropriateness" creates problems where data have to be kept generic because no site has been defined and the expected hydrogeological conditions are not known. Among the main variables to be considered are: the flow rate, the time of leaching, the effects of the temperature and the leachant composition.

Novel materials need a better benchmarking. Existing test methods may not give comparable results with different classes of materials.

Among the data to be measured, the most important is leaching characteristic. Under static leaching conditions, the concentration of dissolved species increases with time, until the solution concentration reaches its solubility limits. But it may not be easy to draw conclusions about the applicability of this type of testing to waste form behaviour in low flow conditions. Surface alteration is a second effect to be considered: monoliths typically react with their service environment so as to form chemically and physically graded structures: reaction is physically inhomogeneous. The waste forms may also be affected by radiation and the products of radiolysis thus affecting the chemical composition of "water" in the waste.

Testing and the extrapolation of short term test data to centuries (or longer) has proved to be very complex. Reliable data on the kinetics of all but the simplest processes are missing. Quality assurance and criteria for acceptance have proven to be another problematical area. Although encouraging progress is reported on non-destructive testing (NDT), additional NDT test methods are required. Criteria for acceptance for final disposal need to be appropriate to the disposal site and activity of the package.

The capacity to model all the effects involved in the dissolution and alteration of the waste form, in conditions similar to the disposal site, and to predict behaviours of cementitious materials used, is the final goal of the research undertaken by some research groups. As described in this document, modelling is still in its developmental stage. Nevertheless it may be the way forward as compression of the time factor is difficult reliably to achieve by accelerated testing. However, it is suggested that the data base for modelling needs to be upgraded and enhanced, and that modellers link to experimental studies designed to verify the key conclusions of mathematical models.

Encouraging progress is reported in the CRP. While many tasks remain incomplete there is a greater understanding and definition of the remaining problems and of approaches and methodologies needed to solve them.

7. COOPERATION ACHIEVED

The CRP was initiated in 2007, based on evaluation of submitted research proposals and final selection of the participating institutions from the respective countries. The participants of the CRP holder of either research contracts or research agreements with the IAEA are as follows:

Australia	Australian Nuclear Science and Technology Organisation (ANSTO)
Belgium	Belgian Nuclear Research Centre SCK·CEN
Brazil	Institute of Energy and Nuclear Research (IPEN)
China	Institute of Nuclear and New Energy Technology (INET)
China	National University of Defense Technologies (NUDT)
Czech Republic	Nuclear Research Institute Řež (NRI)
Egypt	Hot Laboratory and Waste Management Centre (HLWMC)
Finland	Fortum Nuclear Services Oy
France	Commissariat à l'Energie Atomique
India	Bhabha Atomic Research Centre (BARC)
Korea, Republic of	Nuclear Environment Technology Institute (NETEC)
Romania	National Institute of Physics and Nuclear Engineering "Horia Hulubei" (NIPNE)
Russian Federation	A.A. Bochvar High-Technology Research Institute of Inorganic Materials (VNIINM)
Russian Federation	State Unitary Enterprise Moscow SIA "Radon" (RADON)
Serbia	Vinca Institute of Nuclear Sciences
Slovakia	AllDeco
Slovenia	Agency for Radwaste Management (ARAO)
South Africa	Nuclear Energy Corp. of South Africa (Necsa)
Sweden	Swedish Nuclear Fuel & Waste Management Co (SKB)
Switzerland	Paul Scherrer Institut (PSI)
Ukraine	Institute of Environmental Geochemistry
United Kingdom	University of Aberdeen
United Kingdom	University of Sheffield
United States of America	Savannah River National Laboratory (SRNL)

The CRP had the following activities in regard to cooperation:

The first research coordination meeting (RCM) was organized in Moscow from 10 to 14 September 2007 with the purpose to identify objectives of individual projects and to justify R&D programme for the future work. The first RCM was hosted by the Moscow Scientific and Industrial Association "Radon", the venue was at the Hotel "Svetlana" in northern part of Moscow city.

The second research coordination meeting was held from 24 to 28 November 2008 in Romania (Cheile Grădiştei, 24 to 27 November 2008 and Bucharest, 28 November 2008). The CRM resulted with discussion on progress in R&D work, results of bilateral and multilateral cooperation, and establishment of working plan for further research.

The third research coordination meeting was held from 18 to 22 October 2010 at the Bhabha Atomic Research Centre, Kalpakkam, India. Reports of final results of individual R&D work were submitted to the IAEA and presented during RCM. The discussion was held on achievements of the individual projects and on possibility for the implementation. Some novel ideas and approaches were also presented and discussed among participants.

The consultants meeting was held from 25 to 29 October at the Bhabha Atomic Research Centre, Kalpakkam, India as the follow up to the 3rd RCM to consolidate the overall results of CRP.The CRM had the purpose to develop and finalise technical document draft which summarises overall results of the CRP.

The CRP resulted in an active interchange of experiences among leading research groups on the behaviour of cementitious materials in long term storage and disposal of radioactive waste. It has enabled to access valuable information on the underlying science and technology of cementitious materials used radioactive waste management.

This CRP is a good example to the value of the information exchange among its participants and for the results achieved and offered to Member States. The full value of the IAEA CRP programme approach will be reached when either multilateral or bilateral research agreements/contracts among its participants or wider are established as the result of coordinated research and development. In this CRP the bilateral agreement was established between participants from Australia and South Africa, who decided to share their results on commercial basis. Findings of individual works of CRP participants is considered as of high value for utilization of cementitious materials in waste management so it is to be expected that more bilateral agreements between the participants of CRP will happen to continue established cooperative efforts.

8. COUNTRY WORK SUMMARY

8.1. AUSTRALIA

Cementitious materials are used in Australia for conditioning intermediate and low level radioactive waste. In this study a candidate cement based waste form and a series of barrier materials have been investigated using neutron imaging, to characterize the waste form and the barrier materials in assessing their potential to transmit water. Neutron imaging has showed both the pore size distribution and the extent of the cracking that had occurred in the waste form samples. The rate of the water penetration measured both by conventional sorptivity measurements and neutron imaging, was greater than in pastes made from Ordinary Portland Cement. The ability of the cracks to distribute the water through the sample in a short time was also evident. Macro-pore volume distributions for barrier samples, also acquired using neutron tomography, were shown to relate to water/cement ratio, composition and sorptivity data. The study has highlighted the significant potential of neutron imaging in the investigation of cementitious materials. The technique has the advantage of visualizing and measuring, non-destructively, material distribution within macroscopic samples and is particularly useful in description of water movement through the cementitious materials.

8.2. BELGIUM

SCK/CEN in Belgium has investigated chemical durability of cemented NPP radioactive waste (evaporator concentrates and ion exchange resins) submitted to a standard NIRAS/ONDRAF leach procedure taking in total ~450 days. The results were interpreted as effective diffusion coefficients (D_e) for ^{3}H, ^{137}Cs and ^{90}Sr through cement. Standard but shorter leach test procedures (ISO, ANS) are checked in comparison with results for D_e (the time period for which is 90–180 days). The second project tests the waste forms in contact with Boom Clay which is the candidate disposal rock in the underground research laboratory in clay at Mol.

8.3. BRAZIL

IPEN-CNEN/SP in Brazil carried out a research programme to estimate the durability of cement paste under the conditions prevailing in a deep repository for sealed radioactive sources and to understand the long term performance of cementitious materials in repositories. The factors which are considered are material composition: cement types, water/cement ratios, cement additives, environmental factors, exposure to high doses of radiation, higher temperatures and pressures, and attack by aggressive chemicals dissolved in groundwater.

8.4. CHINA (INET)

Spent radioactive ion exchange resin and evaporation concentrates are common radioactive wastes produced in pressurized water reactor (PWR) nuclear power stations. Borate, which is a known retarder for cement curing, is used as a moderator in PWR, therefore borate is contained in both ion exchange resins and evaporation concentrates. Calcium sulfoaluminate cement (CSA or SAC) was studied in radioactive waste cementation in order to improve the efficiency of cementation in China. Waste form formulation comprised CSA cement, waste resins with 50% water contents and water. In order to control the temperature rise caused by hydration of cement in 200L drums, various supplementary materials were tested. Zeolite was selected based on compressive strength tests and centre line temperature rise. In addition, more resins were added to reduce the centre temperature rise. A superior combination was obtained with CSA 35wt.%, zeolite 7wt.%, resins 42wt.% and 16wt.% of water. The microstructures of hydrated OPC, CSA and CSA with different zeolite additions were compared by means of Scanning Electron Microscopy (SEM). From the SEM pictures, the needle type structure spines can be seen in CSA matrices which gradually change into flake-type structure with addition of zeolite. Simulated leaching tests showed that addition of zeolite to CSA reduces the leaching rates of radionuclides significantly. In a 200L matrix test, the centre temperature curve was measured, and the highest temperature was lower than 90 ^{o}C. No thermal cracks were found in the final solidified products. The effect of radiation on compressive strength and radiolysis gas generation was studied for cement solidified forms of various content of ion exchange resin using a Co-60 irradiator up to doses of 10^6 Gy. Data obtained for ion exchange resin loaded samples showed that hydrogen generation under irradiation of 10^5 Gy reached up to 3.5% of the total gas generated and that the radioactivity of spent ion exchange resin shall be limited for long term storage and disposal using High Integrity Containers. Calculations demonstrated however that cement solidification of spent radioactive ion exchange resins in China are not of radiation stability concern. It was concluded that CSA is one of the preferential binding material for ion exchange resins and that the resin loading can be up to 75% by volume for wet resins. It was recommended that the performance requirement for cement solidified radioactive form shall be amended and guidelines for performance characterization should be established. Biodegradation of cement solidified resin shall be investigated and modelling of leaching should be promoted.

8.5. CHINA (NUDT)

NUDT in China has studied physical and chemical processes occurring during the hardening process of contaminated soil cement system and analyses the influence of cementitious materials and processes on properties of concrete such as strength, microstructure, porosity, cracking. OPC was used as the main composition with additives such as super plasticizers, pulverized fly ash (PFA), zeolite, silica fume. The degradation of waste form was analyzed in water at different conditions including water penetration and transport in pores of the concrete, dissolution of different components in the concrete block, the leaching and retention behaviour of radionuclides.

8.6. CZECH REPUBLIC

NRI in Czech Republic focused efforts primarily on investigations of the suitability of advanced cement mixtures, alkali activated cements e.g. geopolymers and polysiloxane mixtures with anorganic fillers to immobilize ion exchange resins from Czech nuclear power plants. Selected Portland cement mixtures developed in the project met all the waste acceptance criteria for low level waste reaching loading capacity about 20 %, but the leach resistance is low. The Cs leach resistance of geopolymers is excellent, but to meet waste acceptance criteria (WAC) and to achieve acceptable loadings (15%), the ion exchange resins must be ground before solidification. Very good results were achieved with polysiloxane matrices both for wet spent ion exchange resins without any previous treatment (loading capacity 35–40 %) and for dried resins (loading capacity more than 70 %). The leaching resistance of solidified products is excellent. The higher price of this material can be outweighed by saving cost for disposal of waste packages and saving repository capacity.

8.7. EGYPT

Leaching characteristics of ^{137}Cs from cementitious waste forms based on different grouts have been assessed to investigate the influence of the additives on the leaching behaviour of the waste matrices. The International Atomic Energy’s Agency (IAEA) standard leach method has been employed. The examination of the leaching data revealed that clay additives to cement are reducing the leaching rate for the studied radionuclide. The controlling leaching mechanism has been studied and the transport parameters were calculated for all studied waste matrices. Simplified analytical models have been derived to predict the Cumulative Leach Fraction (CLF) of radionuclides over the studied experimental period. The simplified research models could be used as a screening tool to assess the performance of the waste matrix under repository conditions.

8.8. FINLAND

Fortum in Finland conducted a number of durability experiments: (i) a full scale experiment with cemented simulated inactive ion exchange resins started in 1980 with waste packages immersed in slowly flowing water in the pond of the Pyhäkoski hydro power plant since 1983; (ii) a half scale experiment with cemented radioactive waste product started in 1987 with waste packages immersed in groundwater taken from the bedrock of the planned repository site. The container is a watertight, superplasticized ready mixed concrete cast in 1980. Even surface moist resin was solidified with blast furnace slag cement. Visual inspection was provided after 1, 3, 5, 13, 15, and 21 years storage period. The full-scale container has withstood the storage extremely well based on the visual inspection and testing. The only external signs of deterioration were rusting of the lifting lugs and shackles and of the thin film of cement paste on the concrete surface of the container. No corrosion was found in the reinforcement steels. The compressive strengths of the cover and side surface concretes, and waste product averaged 63, 82 and 36 MPa, and the carbonation depth varied between 1 and 7 mm. Analysis of the storage water has shown that most of nuclides are below detection limit; Cs slightly above probably due to contamination at the initial stage and not due to leaching.

8.9. FRANCE

The potential of calcium sulfoaluminate (CSA) cement was investigated to solidify and stabilize radioactive wastes containing large amounts of soluble zinc chloride which is a strong inhibitor of Portland cement hydration. Hydration of pastes and mortars prepared with a 0.5 mol/L $ZnCl_2$ mixing solution was characterized over one year as a function of the gypsum content of the binder and the thermal history of the material. Blending the CSA clinker with 20% gypsum enabled rapid hydration, with only very small delay compared with a reference prepared with pure water. It has also improved the compressive strength of the hardened material and significantly reduced its expansion under wet curing. Moreover, the hydrate assemblage was less affected by a thermal treatment at early age simulating the temperature rise and fall occurring in a large volume drum of cemented waste. Fully hydrated materials contained ettringite, amorphous aluminum hydroxide, strätlingite, together with AFm phases (Kuzel's salt associated with monosulfoaluminate or Friedel's salt depending on the gypsum content of the binder), and possibly C-(A)-S-H. Zinc was readily insolubilized and could not be detected in the pore solution extracted from cement pastes, or in their leachates after 3 months of leaching by pure water at pH=7. The good retention of zinc by the cement matrix was mainly attributed to the precipitation of a hydrated and well crystallized phase with platelet morphology (which may belong to the layered double hydroxides family) at early age (≤ 1 day), and to chemisorption onto aluminum hydroxide at later age.

8.10. INDIA

Cement provides a very good matrix for the immobilization of different types of wastes. In India, cementation process has been adopted and it is in use for last four decades. Depending on the waste composition, there is a need to formulate the cement waste matrix. Secondly, improvement of the cement matrix is needed so that the properties such as compressive strength and chemical durability are better. This has been achieved by using different additives/backfill materials during cementation process with various cements like Ordinary Portland Cement (OPC) and Slag Based Cements (SBC). Backfill materials studied include vermiculite and bentonite as well as others. They were evaluated for sorption characteristics, particle size distribution, water equilibration, etc. They were incorporated in the OPC Cement Waste Product (CWP) with various waste compositions. The compositions developed for intermediate level waste (ILW) generated during reprocessing and spent solvent hydrolysis were successfully adopted on plant scale use. Some of the compositions which are being developed are also in the process of adopting in plant. The long term evaluation study of the CWP was carried out at an actual site conditions where CWP in carbon steel drum, plastic drums and bare CWP were disposed of in 2001 and consequently removed in 2010. The parameters such compressive strength, release of activity to the soil, etc. were measured.

8.11. KOREA, REPUBLIC OF

The safe management of radioactive waste is a national task required for sustainable generation of nuclear power and for energy self-reliance in the Republic of Korea. After the selection of the final candidate site for low and intermediate level waste (LILW) disposal in the Republic of Korea, a construction and operation license was issued for the Wolsong LILW Disposal Centre (WLDC) for the first stage disposal. Underground silo type disposal has been determined for the initial phase. The engineered barrier system of the disposal silo consists of waste packages, disposal containers, backfills, and a concrete lining. Main objective of our study in this IAEA CRP was to investigate closure concepts and cementitious backfill materials for closure of silos. For this purpose, characterization of cementitious materials, development of silo closure concept, and evaluation of long term behavior of cementitious materials including concrete degradation in repository environment have been carried out. Overall implementation plan for the CRP comprises performance test for the physic–chemical properties of cementitious materials, degradation modelling of concrete structure, comparison of performance for silo closure options, radionuclide transport modelling considering concrete degradation in repository conditions, and implementation of input parameter database and quality assurance for safety/performance assessment. In particular, concrete degradation modelling study has been focused on the corrosion of reinforcement steel induced by chloride attack, which was of primary concern in the safety assessment of the WLDC. A series of electrochemical experiments were conducted to investigate the effect of dissolved oxygen, pH, and Cl^- on the corrosion rate of reinforcing steel in a concrete structure saturated with groundwater. Laboratory scale experiments and a thermodynamic modelling were performed to understand the porosity change of cement pastes, which were prepared using Ordinary Portland Cement.

8.12. ROMANIA

The mechanical and structural characterization of the radioactive waste conditioning matrix is very important during the final disposal stage in the radioactive waste management cycle. The conditioning products should be a monolith with acceptable mechanical, chemical and physical properties that are maintained over an appropriate time such that the release of radioactivity from the waste form in the environment is minimized. The aim of this work was the XRD phase identification of matrix which simulates the real conditioned radioactive waste and the correlation of phase composition with mechanical performance. The selected matrices for the study were conventional cements with iron precipitate additives (hydroxide and phosphate), mineral additives (bentonite and volcanic tuff) and complexing agents (tartaric, citric and oxalic acids). The results obtained by this analysis gave information about the chemical reactions between the radioactive precipitates and the hydrates–hydrolysis products of the cement.

8.13. RUSSIAN FEDERATION (VNIINM)

In the near future the Russian Federation is planning to use industrially cementation facilities at two radiochemical combines — PA “Mayak” and Mountain Chemical Combine. The CRP included the development of cementation processes of several types of liquid radioactive waste of these enterprisers. The research on cementation of liquid waste from spent nuclear fuel reprocessing at PA “Mayak” allowed to obtain experimental data characterizing the technological process and basic characteristics of produced cement compounds (mechanical strength, water resistance, frost resistance, flowability, etc.) containing different streams of waste (hydrated salt sludges, filter material pulps, mixture of hydrated salt slurries and filter material pulps, tritium liquid waste). Determined optimum technological parameters will allow to produce on industrial facility a cement compound of required quality. Higher flowability was necessary to provide a uniform filling of storage facility compartments. The research has been carried out for the development of cementation technology for pulps from storage tanks of Mountain Chemical Combine radiochemical plant. Cementation of such pulps is a difficult technological task because pulps are of complex chemical composition (hydroxides of manganese, iron, nickel, etc., as well as silicon oxide) and have a relatively high radioactivity. The research programme included study of the influence of sorbent additive types and content on cement compounds leachability, flowability, influence of cement compound age on its mechanical strength, heat generation and others. Testing of the full-scale cementation facility with a pulse type mixer have showed feasibility such type mixers for pulp cementation to prepare a homogeneous cement compound with the required quality. Investigations were performed using both simulated solutions and radioactive pulps.

8.14. RUSSIAN FEDERATION (RADON)

Radioactive waste (RAW) cementation was studied aiming on development of multi-component cement compositions for different waste types immobilization. The RAW were concentrated saline liquid radioactive waste (LRW), concentrated boron containing saline waste, LRW with high surface active substances content and waste with residues, organic LWR, spent ion exchange resins and filter perlite powder, ash residues from solid radioactive waste (SRW) combustion, mixed closely packed and large fragmented SRW. The research programme resulted in defining technological parameters for equipment and cement compositions. Mixing was developed for both continuous and periodic type LRW cementation plants. Mixing, pouring and penetration methods were developed for SRW cementation. Based on equipment parameters, methods and cement grouts were selected to provide the most efficient technological cementation processes.

8.15. SERBIA

Cementation presents a widely applied technique for the conditioning of radioactive and toxic wastes, due to good mechanical characteristics of cement matrix, radiation and thermal stability, low cost and easy operation. Since a main disadvantage of cementitious materials is relatively high leachability, the leaching rate represents one of the most important characteristics of cement–waste compositions. On the basis of the leaching rate, that can be experimentally determined for shorter time periods, a prediction of the percentage of leaching during next 300 years can be made, as well as the estimation of efficiency of immobilization process and comparison with the safety standards that should be reached for storage and final disposal. Leaching studies have been addressed to reduce the leachability of different radionuclides (e.g. ^{137}Cs, ^{60}Co and ^{90}Sr) from immobilized waste matrices by mixing the cement with different materials with significant sorption capacity such as fly ash, silica fume, ilmenite, blast furnace slag, kaolin, zeolites, etc.

8.16. SLOVAKIA

SIAL® matrix is a geopolymer which is the product of inorganic compounds polycondensation. The inorganic SIAL® matrix was subject of study from the atomic level to the level of technological application. Infrared spectroscopy measurement and X ray analysis confirmed that SIAL® matrix is mostly formed by an amorphous phase. It complies with required limits for disposal of immobilized radioactive waste into surface repository. First, leaching of radioactive nuclide Cs-137 and compressive strength of the final product were found. Various remotely operated devices have been designed, manufactured and successfully used for the radioactive sludge and sludge/resins mixture solidification at the Nuclear power plant (NPP) A-1, V-2 in Jaslovske Bohunice, at Mochovce NPP (Slovakia), at Dukovany NPP and at Temelin NPP (Czech Republic). The SIAL® matrix was approved for waste package for sludge/resins mixture by the Slovak and Czech Nuclear Regulatory Authorities.

8.17. SLOVENIA

Slovenian national agency for radwaste management (ARAO) achieved important step at the end of 2009 with adoption of national plan for low and intermediate level waste (LILW) repository, located in Krško municipality near NPP Krško. The selected option was a silo type of near surface facility placed in the saturated aquifer composed of silt with lenses of sand or clay and which extends a few hundred meters deep. Due to challenging geological composition the LILW repository relies on the engineered barriers. Therefore several research study of different cementation materials have been started in order to find sustainable materials for engineered barriers in repository (silo, backfilling, concrete containers,…), assessment of possible degradation processes and provide methodology for the selection of appropriate locally available materials and their combination which can diminish some of the degradation processes. The research was directed in the investigation of 4 concrete compositions and their characteristics (workability, compressive strength), durability analysis (resistance to penetration of water, freeze/thaw resistance, resistance to groundwater), rheology of concrete (heat of hydration, autogenous and concrete shrinkage), protection ability to prevent corrosion of reinforcement and numerical simulation of degradation processes in the cementation materials. The obtained results of measurements have shown that additional research of cementition material should be performed in the directions which have been indicated. No of the tested cementation mixtures provide favourable characteristics therefore improvements in the recipes of binder compositions should be introduced and further measurements are needed.

8.18. SOUTH AFRICA

The durability of concrete is an important issue and the imaging thereof plays a major part in the understanding of the characteristics of concrete. The ability of concrete to withstand the penetration of liquid and oxygen contribute to the durability of concrete. The durability of concrete, can in turn, be quantified by certain characteristics such as the porosity, sorptivity and permeability. For non-destructive analytical quantification of these parameters, neutron radiography was developed and validated against conventional measurements. Results indicated that because the attenuation of the concrete and water differs to a significant degree, the movement of water in ~~a~~ concrete (sorptivity) could be visualized. The neutron radiography results were validated against conventional measurements and excellent correlation was found. To improve the characteristics of current grout/cement matrixes used for the encapsulation of radioactive waste, different cement mixtures CEM 1 (96% OPC) and CEM 5 (mixture of 20% fly ash, 20% blast furnace slag and 60 % cement powder) with the addition of different admixtures, inert fibre material and plasticizers were investigated. With no formal guidance from the waste acceptance criteria (WAC) of the disposal site, it was decided that the following matrix requirements have to be met in order to qualify a possible matrix for radioactive waste immobilization research:

-Total porosity less than 10 % (Implies a compression strength higher than 50 MPa) and

-Sorptivity rate lower than 2.5 grams/hour (Implies pore structure not interlinked and that leaching is less than 10^{-6} g /l).

Results with radioactive waste (excluding organic waste) indicated an admixture of bitumen or asphalt in CEM 1 has the best characteristics and comply with the specified requirement. Treatment of contaminated organic waste which is a non-standard waste stream proved to be difficult and direct disposal is also not an option because many organic liquids are immiscible. Cementation is generally not an option as the cement matrix binds poorly with the organic phase. The absorption of organics such as TBP and oil onto Nochar polymer systems has been demonstrated to be successful with no loss in activity. It has also been demonstrated that after the encapsulation of the polymer (absorbed with organics such as oil or TBP) into the selected cementitious grout, no leaching of radionuclides were observed. The tensile and compression strength of this matrix was improved with the addition of PVA fibres. In this research the effectiveness of chemically bonded phosphate ceramic (CBPCs) stabilization technologies as alternatives to conventional waste immobilization technologies was investigated for the immobilization of ^{129}I (using ^{131}I as a surrogate) and ^{14}C. Performance tests (sorptivity, porosity and leaching tests) were used to determine waste form durability. The results of this research indicate that the properties of the CBPC waste forms when compared to the current cement matrix used at Vaalputs are superior. Excellent retention of iodine in the phosphate ceramic matrices was observed using the ANSI/ANS 16.1 leaching procedure tests, yielding an effective diffusivity rate as low as 10^{-15} cm^2s^{-1}. The excellent performance results of the newly created Zn-P ceramic as an anionic radionuclide immobilization waste form implies that this waste form may also be considered for other “problematic” radionuclides such as ^{99}Tc, ^{14}C and ^{36}Cl.

8.19. SWEDEN

Cement is commonly used as a solidification matrix for wet radioactive waste from nuclear power plants such as ion exchange resins and sludge. Because of that the mechanical and chemical properties of the cement–waste matrix is highly dependent on the chemical properties and the concentration of the waste the recipe used in the solidification process is optimized for each batch of waste through a number of experiments. One highly problematic waste category is evaporator concentrate and ion exchange resins containing boric acid. This is due to that boric acid in some cases has a tendency of inhibiting the solidification of the cement matrix. In this study the influence of artificial ion exchange concentrates and artificial ion exchange concentrates containing boric acid on the compressive strength for cement waste matrices containing boric acid has been studied as a function of time and concentration of the additive. It has been found that for boric acid there is a minimum in compressive strength for a content of about 4 weight% and the experiments showed that at this concentration the cement–waste matrix never cured. This is in agreement with the previous findings which showed that the time for curing is greatly prolonged for specimens with a concentration of boric acid of about 4%. For specimens containing pure artificial evaporator concentrates the compressive strength decreased with increasing concentration of the mixed salts in the concentration range 6 10 wt%.

8.20. SWITZERLAND

In Switzerland it is required to solidify liquid radwaste in order to deposit it in an interim storage or a final repository. In the majority of cases this is realized by cementing the radwaste. In this project the long term mechanical stability and leaching behaviour of a solidified radioactive sludge has been investigated. Following the established procedures, the solidified waste form has been tested first for its compressive strength, water and sulphate resistance as well as for its leaching properties for the relevant nuclides Co-60 and Cs-137 according to the guideline B-05 of the Swiss Federal Nuclear Safety Inspectorate (ENSI). Usually the static leach test with the leaching media demineralized water and gypsum saturated water lasts 150 days with 14 media changes. A part of the solidified sludge samples have been leached for one year and others for 2.5 years with one, respectively two, additional media changes. The waste form, both non-leached, and samples leached up to 950 days, had a compressive strength of about 40 MPa ± 5 MPa, which is four times higher than the guideline value of 10 MPa. As illustrated by the photographs in this report no cracking, spalling or other deterioration was observed even after 950 days leaching. It could be verified that after a longer period of leaching up to 950 days the leach rate tends to a small value, as expected. The amount of leached activity decreases more and more with ongoing leaching time. An exception to this was a slight increase in the leached activity after 950 days in gypsum water. But the absolute value is still about one magnitude for Cs-137 or even two magnitudes for Co-60 lower than the target value of 17.6 % of the authority. The leached samples show no or nearly no carbonation. The zones on the rims of the cylindrical samples with longer leaching times in demineralized water, where Phenolphthalein indicates no colouration (pH below 9), are related to the elution of hydrates, especially calcium hydrate. The layer on the samples after leaching was only calcium carbonate, which could be identified with X ray powder diffraction.

8.21. UNITED KINGDOM (SHEFFIELD UNIVERSITY)

An acoustic emission (AE) non-destructive monitoring technique was devised to characterize the waste–waste form interactions and the degradation potential of encapsulated metals. This technique has been used to evaluate the mechanical performance of cementitious structures with encapsulated metallic waste such as aluminium. Procedures for data analysis were developed to provide information on the Al corrosion processes and analyse their impact on the mechanical performance of the encapsulating cement matrix. AE signals generated as a result of aluminium corrosion in a small size blast furnace slag/ordinary Portland cement sample were detected and analysed. Procedures for AE data analysis were developed to provide information on corrosion processes and analyse their impact on the mechanical performance of the encapsulating cement matrix.

8.22. UNITED KINGDOM (ABERDEEN UNIVERSITY)

The use of cement and concrete to immobilize radioactive waste is complicated by the wide ranging nature of inorganic cementing agents available, the range of service environments as well as the different roles expected of cement. Where concrete construction is used, it is also natural also to use cement in other applications as it minimizes material incompatibility. Thus cement mainly Portland cement has been widely used as an encapsulant for storage, transport and as a radiation shield for waste forms. Relative to other potential matrices, it also has a chemical immobilization potential, reacting with and binding many radionuclides. This chemical potential is essentially sacrificial thus limiting the performance lifetime.

The Portland cement is the most widely used type and benefits from technology transfer from civil engineering research; also of the more than 150 years of experience of its durability and performance in a range of service environments. The origin of the chemical binding potential arises from a combination of mechanisms: chemisorption on cement solids, incorporation by solid solution in cement solids and, at higher concentrations, precipitation of a solubility limiting phase in a calcium rich, high pH environment. These favourable potentials, especially pH conditioning, are, as noted, essentially sacrificial: cement must dissolve or react to maintain these conditions in the course of its service life. However the immobilization potential will also change with time, even in isolation, because cement minerals undergo internal ageing and slow reaction with other materials in the near field. Much research has been conducted, often on an empirical basis, leading to the characterization of these potentials and of their time dependence. Yet the picture which emerges is incomplete and of variable quality. New research is described which, it is expected, will lead to a more scientific basis for the extrapolation of present day cement performance into the future. The high pH of Portland cement matrices has advantages and disadvantages. Portland cement gives excellent protection against corrosion to embedded steel but, on the other hand, it corrodes electropositive metals with evolution of hydrogen. Formation of a high pH "plume" may also spread, affecting the near field, degrading other barriers such as bentonite and affecting the sorptive potential of minerals in the near field for radionuclides. These considerations have led to the search for alternative lower pH cements which are less alkaline. A description of some common types is given. However alternatives present a burden of proof because much less is known about their ability chemically to immobilize waste species and their long term durability relative to Portland cement in a range of natural environments. It is concluded that the most robust of these alternative formulations is based on periclase, MgO, and brucite, $Mg(OH)_2$.

8.23. UKRAINE

Concrete and reinforced concrete are widely used as engineered barriers (containers) for radioactive waste disposal facilities due to their isolating ability, mechanical stability and low cost. Several types of protective reinforced concrete containers for low and intermediate level waste have been designed in Ukraine. Evaluation of these containers for microbial stability is required according to NRC of Ukraine Regulation No.306.608-96. The research was therefore aimed at studying the degradation of the cement material due to microbiological interaction and the possibility of biodegraded cement as an ideal environment for the growth of other microorganisms under waste disposal conditions to satisfy the regulatory requirements. Results from this study indicated that Aspergillus niger induced gluconic and oxalic acids that dissolve portlandite (with a low leaching of calcium) after one year of contact time. This resulted in an increase in porosity, loss in tensile strength biomechanically deteriorated and cracking. XRD analysis identified crystalline precipitates within the biomass on the concrete surface as calcium oxalate dehydrate (weddellite) and calcium oxalate monohydrate (whewellite). The mechanism regarding of the microbiological interaction on the concrete surface can be summarized as follows: Phase 1: Fungi accumulate on the surface of the concrete, thereby degrading the concrete surface by biochemical and biomechanical interactions. When this effect is in the presence of air with available carbon dioxide, the micro fungi reduces the pH of the concrete from >13 to 8.5. During this phase no accumulation were observed in sections where granite aggregates are present. Phase 2: After reducing the pH of the concrete paste during phase 1, and provided that sufficient nutrients, moisture and oxygen are present sulphur oxidizing bacteria start to accumulate on the concrete surface.

The result form this study therefore concluded that fungal biogeochemical activity over a long term period might have negative environmental consequences for the concretes waste containers as fungi (under certain environmental conditions) are able to dissolved the cement matrix resulting in the formation of a biofilm with accumulated structural elements. However, as microbial effects under repository conditions are unknown and difficult to study in a laboratory, no safety assessments conclusions can be made based on results from his study. Long term studies under repository conditions are needed.

8.24. UNITED STATES OF AMERICA

US (DOE) has a complex programme on cementitious materials used in nuclear waste management. Properties are studied such as: (a) hydraulic (hydraulic conductivity, total and transmissive porosity, density; water diffusivity, dissolved ion diffusivity, tortuosity); (b) chemical (retardation factors, chemical reduction and buffering capacity); (c) mineralogy (matrix, radionuclides, other phases); (d) constituent speciation; chemical degradation (e.g. carbonation, oxidation, sulfate attack, rebar corrosion) and (e) structural (physical loads or seismic events). For example, Savannah River National Laboratory (Aiken, SC) worked on grout formulations for SRS reactor facility closures using in situ decommissioning strategies. Fill material characteristic requirements were as follows: flowable; self-consolidating and leveling; minimal segregation / settling; strength > 0.34 MPa (support 50 psi overburden) and > 3.4 MPa after 90 days; low heat of hydration (mass placement). A comprehensive programme was completed on cementitious materials by the Cementitious Barriers Partnership (CBP) which is a multi-disciplinary, multi-institutional collaboration sponsored by the United States Department of Energy (US DOE) Office of Waste Processing. The objective of the CBP project is to develop a set of tools to improve understanding and prediction of the long term structural, hydraulic, and chemical performance of cementitious barriers used in nuclear applications. The documents developed by CBP and published herein (CD attached) are as follows:

(1) Overview of the US Department of Energy and Nuclear Regulatory Commission Performance Assessment Approaches.;

(2) Review of Mechanistic Understanding and Modelling and Uncertainty Analysis Methods for Predicting Cementitious Barrier Performance;

(3) Mineralogical and Microstructural Evolution in Hydrating Cementitious Systems;

(4) Early Age Cracking Review: Mechanisms, Material Properties, and Mitigation Strategies;

(5) Chemical Degradation Review;

(6) Mechanical Damage Review;

(7) Moisture Transport Review;

(8) Review of the Physical and Chemical Aspects of Leaching Assessment;

(9) Review of Thermodynamic and Adsorption Databases;

(10) Review of Approaches to Coupling Physical, Structural and Chemical Mechanisms;

(11) Review of Integrating Programmes and Code Structures Used for DOE Environmental Assessments;

(12) Uncertainty Analysis Methods;

(13) Description of the Software and Integrating Platform Selected for the Cementitious Barriers Partnership (CBP) Project;

(14) Reference Cases for Use in the Cementitious Barriers Partnership Project;

(15) Demonstration of LeachXS™/ORCHESTRA Capabilities by Simulating Constituent Release from a Cementitious Waste Form in a Reinforced Concrete Vault;

(16) Cementitious Barriers Partnership Task 7 Demonstration of THAMES for Microstructure and Transport Properties;

(17) CBP Task 7 Demonstration of STADIUM® for the Performance Assessment of Concrete LAW Storage Structures;

(18) Conceptual design for Phase I of CBP Software Integration;

(19) CBP Code Integration GoldSim DLL Interface.

The above CPB documents are available on the attached CD. The IAEA is grateful to CBP and C. Langton for providing these documents for publication.

LIST OF ABBREVIATIONS

AE	acoustic emission
CRP	coordinated research project
CSH	calcium silicate hydrogel
CWP	cement waste product
FTIR	Fourier transform infrared spectroscopy
ILW	intermediate level radioactive waste
LILW	low and intermediate level waste
LLW	low level radioactive waste
NSDF	near surface disposal facility
OPC	ordinary Portland cement
PHWR	pressurized heavy water reactor
RCC	reinforced concrete construction
SBC	slag based cement
STEM	scanning transmission electron microscopy
SEM	scanning electron microscopy
QA	quality assurance
XRD	X ray diffraction
WAC	waste acceptance criteria

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CONTENTS OF CD-ROM

United Kingdom, Sheffield University:
Acoustic Emission Monitoring of Cementitious Wasteforms.

United Kingdom, Aberdeen University: Cements in Radioactive Waste Disposal.

Ukraine: Assessment of the Biodegradability of Containers for Low and Intermediate Level Nuclear Waste.

United States of America: Use of Cementitious Materials for SRS Reactor Facility In Situ Decommissioning.

UNITED STATES OF AMERICA (additional attachments):

USA Attachment 1. Overview of the US Department of Energy and Nuclear Regulatory Commission Performance Assessment Approaches.

USA Attachment 2. Review of Mechanistic Understanding and Modeling and Uncertainty Analysis Methods for Predicting Cementitious Barrier Performance.

USA Attachment 3. Mineralogical and Microstructural Evolution in Hydrating Cementitious Systems.

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USA Attachment 16. Cementitious Barriers Partnership Task 7 Demonstration of THAMES for Microstructure and Transport Properties.

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USA Attachment 18. Conceptual Design for Phase I of CBP Software Integration.

USA Attachment 19. CBP Code Integration GoldSim DLL Interface.

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