

Reactions in cement encapsulated nuclear wastes: need for toolbox of different cement types

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Reactions that occur between a radioactive waste and a cement matrix being used for encapsulation can compromise the integrity of the resulting wasteform. The present paper describes some of the interactions that can occur within Portland cement based systems. It highlights the fact that to achieve successful encapsulation of the wide range of waste types that make up the legacy or historic wastes present in the UK, a toolbox or formulary of different cement systems with differing chemistries is needed. Some potential alternative cement systems are discussed.

Keywords: Cement, Encapsulation, Immobilisation, Radioactive waste

Introduction

One of the biggest problems facing the nuclear industry worldwide is the generation of a waste that has the potential to pollute the environment for years to come if not properly treated. For many years, much of that waste has simply been stockpiled and left presumably for future generations to deal with. Whilst in the UK most of the operational waste is now handled either by cementation or by vitrification, there remain large amounts of historic or 'legacy' wastes carried over from the start of nuclear activity, often stored under less than satisfactory conditions. Before there is any likely change in public attitude towards nuclear power generation, and to gain public acceptance that nuclear power is a viable option for the future, the industry must show that all of these wastes can be dealt with.

Radioactive wastes vary considerably in terms of their activity level, half-life, volume and even nature (scrap metal, rubble, oil, etc.). Treatment and final disposal solutions must be adapted to the type of waste concerned, in order to overcome the risk that radioactivity will be released to the environment. The radiological hazards can be assessed on the basis of two main parameters: activity level, indicating the toxicity of the waste, and radioactive half-life, which measures how long the waste will constitute a problem. Wastes are classified into three categories according to their level of activity: low level wastes (LLW), intermediate level wastes (ILW) and high level wastes (HLW).¹ In the UK cementation is the preferred option for turning ILW and LLW into monolithic wasteforms suitable for storage and ultimate disposal.

Cements have been used for encapsulation of radioactive wastes for a number of years and there are several

extensive reviews detailing the requirements and properties of cementing systems largely based on Portland cement.²⁻⁵ Cements offer a number of attributes that make them very suitable for encapsulation and immobilisation. They are inexpensive and readily available, can be easily prepared and used in remote operations, and can be produced in the form of a fluid grout able to penetrate complex waste shapes. They also assist immobilisation of radionuclides by acting as a diffusion barrier, providing sorption and reaction sites and maintaining a high pH which in turn decreases radionuclide solubility. Finally, cements provide a radiation stable binder and have controllable permeation and diffusion characteristics over a wide range via selection of constituents and components.

Encapsulation v. immobilisation

There is very often confusion as to whether a given waste is immobilised or encapsulated. It is easy to visualise the encapsulation of a waste such as a metal where it is clear that there is going to be little interaction of the bulk of the material with the cementing matrix. However, for slurries such as iron flocs onto which actinide species are adsorbed, or BaCO₃ containing ¹⁴C that has been captured from off-gases, the distinction is less clear as reactions are shown to occur. Wastes such as concentrated salt solutions are likely to need treatment to immobilise the active species before encapsulation.

In encapsulation, the waste is surrounded with a physical barrier of cemented material which serves to isolate the waste from the environment. Little or no chemical interaction of waste is expected to occur with the matrix. On the other hand with immobilisation some interaction between the waste and matrix may occur, where the waste is precipitated within the matrix by a chemical reaction or incorporated within the matrix structure as the cement sets. Because in many cases it is difficult to define which is happening, the term

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solidification and stabilisation is increasingly used to describe the total treatment.⁶

Reactions with cementing matrix

Ordinary Portland cement (OPC) and its composites are the most widely used cementing matrixes. Portland cement is made up of four main components, tricalcium silicate C_3S (50–60%), dicalcium silicate β - C_2S (20–30%), tricalcium aluminate C_3A (8–12%) and an iron containing phase C_4AF (C_5CaO , S_5SiO_2 , $A_5Al_2O_3$, $F_5Fe_2O_3$, H_5H_2O). These hydrate largely independently and at very different rates. Numerous textbooks⁷ detail the manufacture and hydration of the phases in OPC and these will not be considered here.

Two types of waste/cement matrix interactions must be considered. The first is where the interaction can directly affect the hydration reaction of the cement, either by acceleration or retardation. A number of soluble wastes do little other than affect the setting time and become incorporated within the binder. The second series of reactions are those that continue to occur within the hardened matrix and can lead to loss of integrity of the wasteform and hence long term durability.

Chemical reactions during OPC hydration

The hydrated calcium silicate formed is amorphous and has variable composition depending on the stage of hydration. It is usually given the form C–S–H to represent the variation in the Ca/Si ratio during hydration as well as in the amount of water associated with it. Much work has been conducted on the form of the C–S–H binder.⁸ Along with C–S–H, $Ca(OH)_2$ is also formed. With the small amounts of alkalis present this ensures that the pH of the internal pore solution is high, usually in excess of 13.

Composite cements: pozzolanic reaction

The hydration of cement is an exothermic reaction. Each phase has a different heat of hydration, in the sequence $C_3A > C_3S > \beta$ - $C_2S \geq C_4AF$. While OPC can be used directly for waste encapsulation, one major disadvantage is that when it is used in large masses, the temperature rise due to the heat of hydration can be very high, giving rise to severe thermal stresses. Heat generation of around 230 kJ kg⁻¹ is normal for OPC, resulting in temperatures in excess of 100°C in the centre of drums,⁹ which can lead to cracking. To reduce the temperature rise, pozzolans such as blast furnace slag (BFS) and pulverised fuel ash (PFA) are used at high replacement levels. These react with the $Ca(OH)_2$ produced from C_3S hydration to form additional C–S–H in a reaction that is low heat emitting. BFS also functions as a latent hydraulic cement, its hydration activated by hydroxides and sulphates to form additional C–S–H. The use of large amounts of BFS has the two benefits of decreasing matrix permeability as well as reducing the internal pH to 12.0–12.5, down from the value around 13.5 normally encountered with pure OPC. PFA functions in a similar way but without its own hydraulic activity. The resulting C–S–H formed from pozzolans and without $Ca(OH)_2$ present is chemically more durable and offers improved resistance to permeation by reactive species. As a consequence, composite cement systems where large amounts of cement are

replaced with BFS or PFA are the preferred options for most encapsulation operations in the UK.

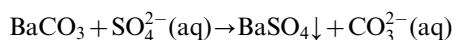
Reactions of wastes with hydrating cements

Wastes containing high levels of soluble species such as phosphates,¹⁰ borates¹¹ and metal ions such as zinc¹² and tin¹³ show marked retardation of the cement hydration reaction. If these species are present in large amounts, then the setting reaction will be affected and low strength wasteforms may result. In an extreme case the cement may not set, although for zinc, where the delay may be several weeks, hardening will eventually occur. Most retarding species precipitate insoluble Ca salts such as $CaZn(OH)_6 \cdot 2H_2O$ ¹⁴ or $CaSn(OH)_6$.¹⁵ These precipitates coat the outside of the cement particles and slow the diffusion of ions and water. Provided the concentration does not completely inhibit hydration, setting and hardening will eventually continue. Elements such as Sn and Zn become incorporated in the silicate binder with time. There is evidence that treatment of soluble zinc salts with sodium phosphate¹⁶ prevents retardation, while lime treatment of phosphates and borates¹⁷ can reduce retardation by precipitating insoluble calcium salts before the wastes are added to the cement. The caesium ion Cs^+ is one of the ions that proves difficult to encapsulate in cemented wasteforms as its salts are so soluble. Hoyle and Grutzeck¹⁸ showed that availability of soluble Al in a hydrating cement system from PFA provided a matrix in which the Cs^+ was adsorbed.

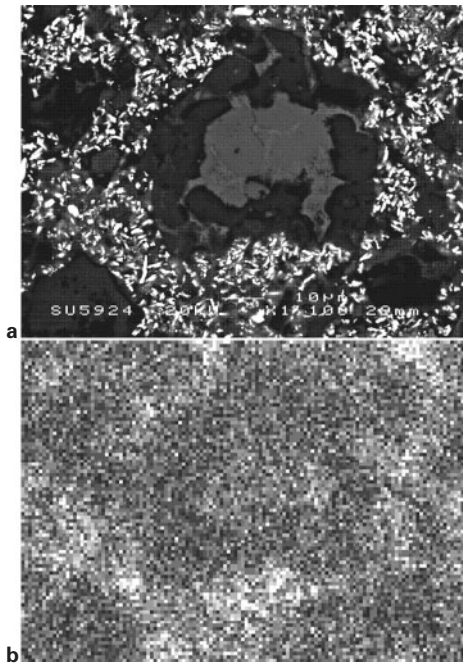
At the Immobilisation Science Laboratory, University of Sheffield, UK, investigations into the hydrated cement matrix are being undertaken to understand the extent and mechanism of any interactions that occur and to determine whether they will affect durability.

Encapsulation of $BaCO_3$

In fuel reprocessing at THORP at Sellafield (Cumbria, UK), ¹⁴CO₂ released from acid dissolution of fuel is scrubbed from the gas stream with NaOH and precipitated with $Ba(NO_3)_2$ as $BaCO_3$. This waste stream is concentrated to a slurry, mixed with a BFS composite cement system and allowed to harden. Previous work by the present author and collaborators¹⁹ shows that far from being unreactive, the $BaCO_3$ reacts with the hydrating cement, influencing the other reactions that occur. During hydration, the normally insoluble $BaCO_3$ ($K_{sp} = 2.6 \times 10^{-9}$) reacts with any soluble sulphate present to form the least soluble species, $BaSO_4$ ($K_{sp} = 1.1 \times 10^{-10}$). This reaction removes all soluble SO_4^{2-} from solution, releasing soluble carbonate anions:



Element mapping (Fig. 1) shows that $BaSO_4$ precipitates around the outer surface of the cement grains hindering hydration, as shown by isothermal calorimetry. It has also been found by isothermal calorimetry that $BaCO_3$ accelerates the hydration of BFS. Possibly the fine $BaCO_3$ particles provide a site on which nucleation and growth of C–S–H can occur. Fortunately, the carbonate ions released do not remain in the pore solution but are incorporated into a calcium monocarboaluminate



1 a BSE image of OPC with 30%BaCO₃ and 0.37 water/solids ratio cured for 90 days at 20°C; b elemental map for sulphur showing distribution around hydrating cement grains

(AF_m) phase, which fixes them so they cannot readily be leached.

Iron flocs

Actinides are strongly adsorbed onto hydrous iron oxides.²⁰ In the Enhanced Actinide Recovery Plant (EARP) at Sellafield, iron flocs are produced in several processing lines to absorb the low concentration of actinide species. These flocs are dewatered to give colloidal slurries with solids content around 15% which can then be successfully immobilised in an OPC/PFA composite, but only after pretreatment with Ca(OH)₂ to ensure the monolith formed does not crack on curing.

In current work,²¹ Ca(OH)₂ has been shown to react rapidly with the floc within the first few hours, forming small amounts of the iron ettringite analogue, Ca₆Fe₂(SO₄)₃(OH)₁₂·26H₂O, and a phase similar to Fe₆(OH)₁₂CO₃ as the Ca(OH)₂ carbonates. Without pretreatment, any Ca(OH)₂ released from the cement will react with colloidal floc particles and not the PFA, so giving a very weak wasteform with high porosity. One of the phases formed is a non-binding hydrogarnet, siliated katoite, C₃(A,F)SH₄. It is likely that this species is heavily iron substituted owing to the large amount of colloidal iron hydroxide present, some of which will be incorporated into the hydrogarnet.

These two examples serve to highlight the fact that when any compound is encapsulated, reactions are likely to occur with the hardening matrix. All possible reactions that can occur in the pore solution must be considered when assessing long term durability. The least soluble species will be precipitated from the ions present in solution regardless of their necessity for a particular reaction, while in the case of the iron floc, additional Ca(OH)₂ is needed to ensure the expected pozzolanic reaction can occur. Ongoing work is being carried out to characterise the pore solution chemistry in

these high replacement composites which differ from construction cement blends.

Degradation of cellulose

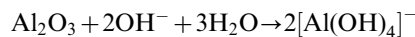
Low level waste (LLW) is made up of a wide variety of materials used in the processing of fuel. This waste can include articles of clothing as well as gloves and papers, etc. Many of these organic materials contain cellulose. In the highly alkaline environment of the hydrated OPC matrix cellulose degrades over the first few hours, ultimately forming acids such as isosaccharinic acid.²² While the cellulose breakdown products can affect the setting of cement,²³ the major concern is solubilisation of actinide species through complexation.²⁴

Reactions in hardened cement

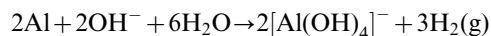
While some wastes can affect hydration so preventing the formation of a stable and durable wasteform, there are several wastes where a reaction can occur within the hardened paste. In this case it is the presence of alkaline pore water that continues to drive the reaction. These ongoing reactions are of major concern for encapsulation of wastes as it is not clear how long the wasteform will remain intact. A good example is ongoing corrosion of metals.

Metals in encapsulated wastes

Reactive metals such as aluminium and magnesium make up a significant proportion of the legacy or historic wastes in the UK. Even the pH reduction provided by siliceous additions such as BFS and PFA is not enough to prevent corrosion of aluminium. In the alkaline environment of hydrating OPC, the normal oxide layer that coats the highly electropositive metal does not provide the necessary corrosion protection expected of aluminium, leading to the reaction:

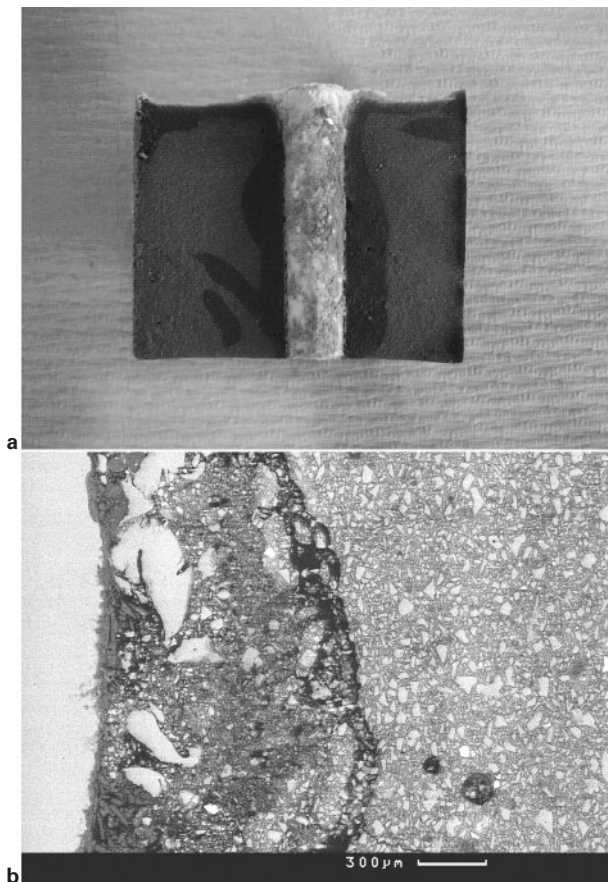


This leaves the bare metal open to corrosion:



In previous studies,²⁵ aluminium corrosion has been shown to be slower in composite systems than in OPC, with the corrosion rate highly dependent on the purity of the aluminium and pH. An impure aluminium (alloy 1050, 99.5%Al) reacts very much faster than very pure Al (99.999%), the impurities providing sites at which pitting corrosion is initiated. While overall the cement hydration reaction does not appear to be affected, considerable porosity is generated around the corroding metal owing to the evolution of hydrogen (Fig. 2). Any soluble Al species generated at the surface of the aluminium migrates through this pore space to the hydrating cement matrix and becomes incorporated into the silicate products forming a new compound, Strätlingite, C₂ASH₈, indicating that the corrosion products do interact with the cementing matrix. As the cement hardens, diffusion of water and hydroxide ions to the aluminium surface is slowed and the corrosion rate decreases. Considerable corrosion of aluminium takes place before setting occurs, with the resultant hydrogen evolved creating voids around the aluminium (Fig. 2).

As the hydration reaction proceeds, the pH at the aluminium surface drops, precipitating Al(OH)₃ as



2 a corrosion of Al in 9:1 BFS/OPC after 90 days at 20°C; b Al/cement interface: Al metal on left, porous region centre, cement on right

bayerite. The corrosion product is less dense than aluminium, so its formation is expansive, causing internal stresses which can ultimately crack the grout.

Cementation of ion exchange materials

Many radioactive species are present in dilute concentration, so cementation of these very dilute wastes is not efficient and concentration is needed. Selective adsorbents are used to concentrate ions, such as clinoptilolite, a natural zeolite which will selectively extract Cs^+ and Sr^{2+} . New types of adsorbents such as IONSIV,²⁶ a crystalline titanosilicate ETS-10, or SAMMS,²⁷ self-assembled monolayers on mesoporous supports, can be formulated to target specific ions and provide concentration and removal of these from low concentrations in high salt content solutions. These materials are usually handled in the form of pellets and a suitable method of incorporating them into a suitable monolithic wasteform has yet to be devised.

Ongoing work²⁸ has shown that in OPC based composite systems, clinoptilolite will interact with the alkaline pore solution. Zeolites are known to function as pozzolans when finely ground.²⁹ While the general shape of the clinoptilolite particle remains, its structure is partially destroyed and Cs can be leached from the cemented matrix. The stability in alkaline solutions of SAMMS must be questioned although IONSIV is likely to be stable. Nevertheless, this reaction with the cementing matrix does raise the question of how selective adsorbents will react within a strongly alkaline solution as well as the fate of the adsorbed species.

Search for alternative cement types for encapsulation

Because the high pH of an OPC composite system creates problems with metals such as aluminium and selective adsorbents such as zeolites, alternative cementing systems are needed which have different chemistry. These systems could also be suitable for other wastes if the chemistry is compatible.

In the OPC based systems described above, high water/solids ratios are used to ensure sufficient workability. The degree of reaction of pozzolans is limited owing to the low levels of OPC, so high levels of unreacted water are present as a highly alkaline pore solution. Current work by the present author's group³⁰ using proton NMR relaxometry to study the types of water present in OPC slag blends indicates that after 90 days, typically around 15% of the total water remains unbound and is held in capillary pores in a 9:1 BFS/OPC formulation. For a 3:1 BFS/OPC blend, most water becomes bound or is at least held in gel pores. For the 9:1 blend, little change in hydration occurs after 14 days, indicating that hydration has stopped. The pore solution remaining contains soluble ions which will move if a concentration gradient can be established such as occurs in leaching. Soluble ions will readily migrate if there is sufficient permeability and they are not bound. In metal corrosion, where transport of hydroxide ions and water to the metal surface drives the corrosion, pH and permeability play important roles in determining the rate at which corrosion will occur. Thus an alternative cementing system where free water and/or pH can be reduced would be of considerable benefit in reducing corrosion.

What are the requirements for a cement system for encapsulation of wastes? A number of alternative cement systems have been used for various, usually specialised, construction purposes.³¹ For several, their properties are reasonably well known and they offer different chemistries to calcium silicates. The requirements of a cementitious system for encapsulation are somewhat different from those needed for construction purposes, particularly as far as early strength is concerned. Among the key parameters needed for an encapsulation system are: an ability to incorporate waste and harden; fluidity of initial cemented mix and potential for remote mixing; low permeability when set; resistance to water; low temperature rise on setting; workable setting time; low free or unbound water when setting reaction is complete; low internal pH to avoid ongoing reactions such as corrosion; long term durability. Systems which fit most of these parameters include aluminous cements, phosphate cements, calcium sulphoaluminate cements and alkali activated silicate systems. In studies in Spain examining suitable cements for concrete at the El Cabril repository, concern about long term durability of new cementing systems meant that only systems which had an experimental track record of more than 25 years were thought worthy of consideration.³²

Calcium aluminate cement

Calcium aluminate cement (CAC) was first developed in France in 1914 as an alternative construction material to Portland cement to provide added durability in

chemically demanding situations. The hydrated matrix that forms has lower porosity and a greater resistance to chemical attack, particularly as regards sulphate and carbonation. This cement has been called high alumina cement, but the term calcium aluminate cement is to be preferred since specialty cements with very much higher alumina contents are produced for refractories.

Modern CAC (ciment fondu) is made by fusing limestone and impure bauxite, often incorporating a significant amount of iron as fluxing agent. The setting time of CAC is comparable with that of OPC but its strength gain is more rapid, so that after 24 h of curing the compressive strength is comparable with that of OPC after about 28 days. The main cementing phase present is monocalcium aluminate with small amounts of $C_{12}A_7$, but iron is often present as C_4AF .

CACs have potential advantages for encapsulation of wastes because they do not liberate Portlandite $Ca(OH)_2$ on hydration and so the pore solution has a lower pH, although it is still alkaline. Two issues must be addressed for its potential use for encapsulation. The first is to avoid (or design for) the volume and strength changes that accompany the process known as conversion, where the metastable hexagonal hydrates initially formed, CAH_{10} and C_2AH_8 , transform into the thermodynamically stable cubic phase, hydrogarnet, C_3AH_6 and $Al(OH)_3$. The rate of conversion depends on several factors such as the original hydration temperature and subsequent exposure conditions. The conversion reaction results in a more porous matrix which contains free water, since the hydrogarnet formed is denser and binds less water. The second issue is that the hydration reaction and rapid strength development are accompanied by a considerable evolution of heat, so this cement is unlikely to be directly suitable for use in large masses unless methods of reducing the heat output are developed.

One way of addressing both these factors is to replace some of the CAC by BFS. Majumdar *et al.*³³ showed that by using equal amounts of CAC and BFS, concrete cured at either 20 or 38°C increased continuously in compressive strength over a year, in contrast to control samples that showed decreases associated with phase conversion. Mixes incorporating BFS and also silica fume^{34,35} prevent the conversion reaction and form Strätlingite, C_2ASH_8 . A similar cement was devised by Sugama *et al.*³⁶

Although not used currently for waste immobilisation, some studies^{34,37} have considered the potential of CACs for nuclear repositories. Majumdar *et al.*'s work³³ could be extended to include much higher contents of BFS, however heat evolution, hydrate formation and microstructure development for a new type of composite cement must first be determined. One advantage of the matrix is the reduced pH of any pore solution. Toyohara *et al.*³⁸ showed that CACs could incorporate iodide into the hexagonal hydrate structure forming $C_3A.CaI_2.12H_2O$. The reaction was reversible and dependent on I^- concentration, but this does emphasise the potential for anion retention.

Phosphate cements

A number of cements based around the use of phosphates rather than silicates as binders are becoming more widely investigated. These cements tend to

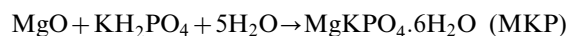
function at very much lower pH than the silicate based cements, offering an alternative to alkaline systems as they do not require the use of an alkaline activating system. Cations that form suitable phosphate cementing systems include magnesium, calcium and zinc.

Magnesium phosphate cements

Magnesium phosphate cements have been developed for rapid setting and early strength gain, usually for special applications such as repair of pavements and concrete structures or for resistance to certain aggressive chemicals. Commercial magnesium phosphate cements typically reach a compressive strength of about 13.8 MPa after 1 h, with an ultimate strength of 55 MPa, and exhibit good durability.³⁹

The binder is formed by an acid–base reaction of magnesium oxide with a soluble acid phosphate, such as ammonium phosphate, either as the mono- or dibasic salt. This results in an initial gel formation followed by its crystallisation into an insoluble phosphate, mainly magnesium ammonium phosphate hexahydrate, $NH_4MgPO_4.6H_2O$. To control setting, the magnesium oxide used in this system needs to be unreactive, either hard or dead burnt MgO, and is normally used in conjunction with a set retarder, typically either borax or boric acid, to afford a workable setting time. In contrast to magnesium oxychloride (MOC) and magnesium oxysulphate (MOS) cements, the phosphate cement system has good water and freeze/thaw resistance.

A similar system, extensively studied at Argonne National Laboratory, is now marketed for the purpose of waste remediation as 'Ceramicrete'.^{40,41} In this system, magnesia and monopotassium dihydrogen phosphate are used which react as:

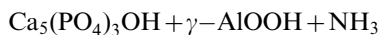
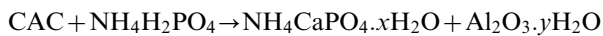


One disadvantage of the system is that temperatures around 80°C can be reached with the use of potassium dihydrogen phosphate and fused MgO in large volumes, but this can be reduced with the addition of a siliceous fly ash. Many metals are precipitated as insoluble phosphates making this an ideal matrix for encapsulation of many species, and high levels of many salts can be incorporated without problems. Addition of sulphides ensures that metals such as Hg, As or Cr are precipitated as insoluble sulphides and encapsulated during the magnesium phosphate formation. The pH within the system varies from around 4 to 8 depending on the stage of reaction. Full scale active trials have proved this system to be suitable and leaching trials indicate that most species are retained.

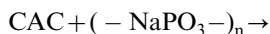
Calcium phosphate cement

An alternative approach was taken by Sugama *et al.*⁴² In an ongoing investigation at Brookhaven National Laboratory into a cementing system suitable as a carbonation resistant geothermal cement, a system was developed based around CAC with the addition of soluble phosphates. The reaction is still the same acid–base type as noted for the magnesium phosphate systems, but in this case the base is CAC and the product is a calcium ammonium phosphate. Under hydrothermal conditions, hydroxyapatite and amorphous boehmite were formed above 200°C according

to the reaction sequence:



Health and environmental concerns with ammonia emissions led to the use of sodium polyphosphate, when an analogous reaction occurred:



This system could be treated hydrothermally and converted to hydroxyapatite which is then largely unaffected by carbonation. In a final stage, addition of a class F fly ash was used to improve strength and density characteristics. Upon hydrothermal treatment, in addition to hydroxyapatite, analcime, $\text{NaAlSi}_2\text{O}_6 \cdot \text{H}_2\text{O}$ was also formed. This patented technology, known as 'ThermaLock', has been used successfully for cementing in several geothermal wells.

CSA cements

Cements known as calcium sulphoaluminate (CSA) cements are manufactured on a large scale in China (>1 Mt per annum) for construction purposes, with smaller amounts made elsewhere in the world. A mixture of limestone, an alumina source and gypsum (or anhydrite) is heated in a rotary kiln to about 1300°C giving a clinker which contains the phase yeelimite $\text{C}_4\text{A}_3\text{S}$. In the presence of anhydrite or gypsum as activator, this phase hydrates rapidly to form ettringite $\text{C}_3\text{A} \cdot \text{CaSO}_4 \cdot 32\text{H}_2\text{O}$ along with $\text{Al}_2\text{O}_3 \cdot n\text{H}_2\text{O}$. Because the clinkering temperature is lower than that required for Portland cement and the clinker is easier to grind, the cements are often classed as low energy cements with reduced CO_2 emissions.⁴³

These cements normally contain only small amounts of silicates so $\text{Ca}(\text{OH})_2$ is not formed on hydration and the internal pH is lower than with OPC, typically 10.5–11. Provided the gypsum content is high enough, any $\text{Ca}(\text{OH})_2$ formed will react with the $\text{Al}(\text{OH})_3$ to form further ettringite. One real advantage is that the formulation can be varied to form large amounts of ettringite, which is suitable for incorporating a large range of ions within the ettringite structure making them very suitable for the stabilisation of waste materials.⁴⁴ One issue is the rapid setting reaction and strength development which is likely to create problems with heat evolution, although work quoted by Zhou⁴⁵ indicates the total heat involved is less than that from OPC.

Work by the present author's group⁴⁶ has shown that grouts can be prepared with high water/solids ratio mixes which exhibit greater fluidity than OPC composites but without bleeding. The main feature is that virtually no Al corrosion occurs, maybe as a result of a combination of pH and a lack of free water.

Alkali activated systems

Two different alkali activated silicate systems are currently receiving considerable interest worldwide as cement manufacturers seek to reduce CO_2 emissions. Alkali activated slag (AAS) was developed in the 1950s

in the USSR⁴⁷ and is being intensively investigated. It is typically made from ground granulated blast furnace slag and a soluble alkaline component, usually sodium silicate. Compared with the OPC system, AAS offers reduced water demand, lower permeability, lower heat of hydration and good resistance to chemical attack. AAS has been successfully used as a matrix for immobilising Hg^{2+} , Zn^{2+} , Cr^{6+} , Cd^{2+} , Pb^{2+} , Cs^+ and Sr^{2+} from various wastes.^{48,49}

Current work being conducted by the present author's group on activation with near neutral pH salts Na_2SO_4 and CaSO_4 has shown that a satisfactory wasteform can be generated from a blast furnace slag considerably finer than that conventionally used in waste encapsulation but with a significantly lower pH.⁵⁰ These systems are similar to the super-sulphated cements⁵¹ popular before the 1980s, but do not include the addition of OPC. These systems set and harden slowly. The measured internal pH is low at around 11, and experiments being conducted show there is limited corrosion of aluminium. The matrix also appears to be comparable to OPC for retaining ions such as Cs^+ and I^- , two of the most difficult species to immobilise in cemented matrixes. While there is more work to be done on this system, it offers a chemistry with pH lower than in OPC systems, so active metal corrosion is reduced.

Geopolymers

An alternative cementing system based on aluminosilicate polymers (inorganic polymers sometimes known as geopolymers) was developed by Davidovits in the 1970s.⁵² This system proves to be suitable for cements needed in chemically demanding situations. The ingredients in the initial formulations were a soluble alkali silicate and a reactive aluminosilicate precursor such as calcined kaolinite or metakaolinite. Strength development is much more rapid than in OPC systems, giving a product with moderate strength (15–20 MPa within 6 h and around 80 MPa at 24 h). As the binder is not a hydrate, the system exhibits high thermal stability (samples have been tested to 800°C). The water is held in non-connected pores, possibly associated with alkali ions. Ongoing work has shown that a range of reactive precursors such as blast furnace slag^{53,54} or PFA⁵⁵ can also be used, thus lowering the cost of the system, but these require heating at temperatures up to 80°C to initiate curing. However, depending on the calcium content, some of these products may be regarded as similar to alkali activated slags, in which case calcium silicate hydrates form as part of the binder. The range of materials that can be used as a precursor indicates the flexibility to incorporate a range of waste materials in a medium that ultimately does not rely on a hydrate matrix for strength, as the binder is a three-dimensional amorphous aluminosilicate. The role of calcium in the geopolymer system is not well understood, and problems with short setting times tend to be recorded for systems high in calcium. One of the major problems with this system is that each starting material is different and setting and hardening characteristics need to be established empirically.

Although the binder in these systems is not a hydrate, aqueous alkali silicates are used as activators and the final fate of the water is still undecided. The best evidence to date suggests that it is held in small

non-interconnected pores. Water loss on heating occurs only slowly but steadily up to around 600°C and indicates significant porosity. The internal pH remains extremely high owing to the excess sodium hydroxide needed to solubilise the aluminosilicate precursor, which is not incorporated into the geopolymers as a counteraction.

Work by van Jaarsveld and van Deventer⁵⁶ and Davidovits⁵⁷ discussed the possibility of immobilising radioactive waste with these materials. Recent work at ANSTO⁵⁸ also indicates that Cs and Sr are retained in the system. Work in Sheffield⁵⁹ suggests that while cations such as Cs are retained, anions such as PO_4^{3-} and CrO_4^{2-} are not.

Further work is needed to gain an understanding of the hardening mechanism as well as to determine the long term durability of such a new system. The extent of reaction that occurs is hard to measure as it is clear that the unreacted precursor acts as a centre for polymerisation and so is well bonded into the system. Experimental trials⁶⁰ indicate that concrete made using this binder system does not suffer the effects of acid attack or carbonation. Industrial trials show that this material can be handled and manufactured on a large scale, but problems do arise with either very short setting times or long delays in hardening, some of which can be reduced by changing formulations. The fundamentals of how the setting and curing mechanism occur are not well defined, and at present for each precursor a suitable formulation must be determined empirically.

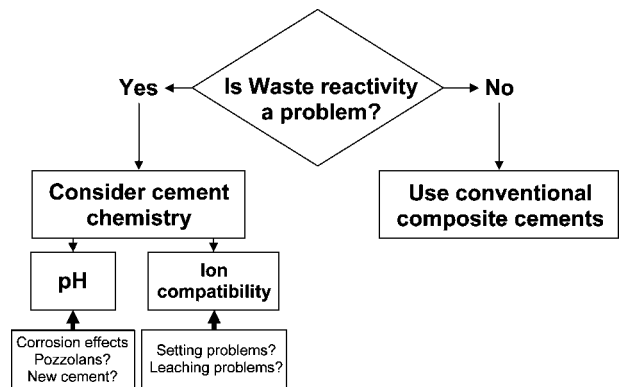
Other cementing systems

A number of other cementing systems such as Sorel cements are used for specialist applications, but only those where a good documented history of durability is available and which are water stable have been considered. It is unlikely that any system not stable in water when hardened will exhibit sufficient durability to be considered for a wasteform. Where a component of any system is soluble, the curing regime must include containment of the mix to minimise diffusion of an active ingredient to the surroundings. Similarly, a system that relies on diffusion of a chemical into the matrix to harden it, for example carbonation, is also likely to be unsuitable for preparation of a wasteform with long term durability, as the reaction may not reach completion.

Concluding remarks

The selection of a suitable cementing system for encapsulation and immobilisation of radioactive waste is a complex task. With any system there are several key parameters that must be addressed to ensure ultimate durability. While the most important are chemical reactivity and likely interactions, physical properties such as the temperature rise during setting and associated thermal stresses, and the ability to process a system with issues such as fluidity, setting time and processing conditions also play a key role in the selection of a suitable cementing formulation.

When designing encapsulation of any particular waste, a flowchart similar to that shown in Fig. 3 needs to be followed to be able to select a suitable cementing system. Apart from the obvious chemical reactions that



3 Flowchart for selecting cement system from toolbox or formulary of different cement types

can occur, such as corrosion, any reaction of the encapsulated waste with the encapsulating matrix must be understood and allowed for. For example, containment of the $^{14}\text{CO}_3^{2-}$ anion from BaCO_3 within the cementing matrix is essential. Zeolites and other specific adsorbents being considered for concentration of low levels of ions from radioactive waste solutions need to be encapsulated into a monolithic form. How these adsorbents will react in an encapsulating matrix and what the fate of the adsorbed species will be is a consideration that often cannot be assessed without experimental work, especially if composite systems are used. In this case pH is a factor that must be considered as it is for reactive metals.

The temperature rises associated with the large masses of any cemented matrix also have to be taken into consideration. The use of additives such as PFA and BFS modifies the hydration reactions but can reduce temperature rise. For many cementing systems, including those composites with OPC, changes in the microstructure occur when they are heated to elevated temperatures, and these changes must be considered when estimating durability. This temperature rise can however be used to advantage. Autoclaved OPC/quartz products are known to be very stable and offer some advantages such as improved strength and decreased permeability, as well as the hydration reaction going to completion over a shorter time.

It is unlikely that any one cementing system will be suitable for all waste types. Industry is therefore likely to need a toolbox or formulary of several different cement systems with different chemistries to cover the complex mixture that makes up legacy waste.

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