

# Fundamental aspects of cement solidification and stabilisation

F.P. Glasser

*Department of Chemistry, University of Aberdeen, Meston Walk, Old Aberdeen, Aberdeen AB9 2UE, UK*

---

## Abstract

Cement matrix materials intended for immobilisation vary considerably in their formulation. It is often economically and technically advantageous to add blending agents: e.g. slag and fly ash. These affect the chemical, mineralogical and microstructural constitution of the system. However, blending agents react slowly with the result that the physicochemical properties of the matrix are time dependent. This affects especially conclusions which might be reached from accelerated short-term leach tests: the intrinsic performance of blended cement matrices improves with maturation.

The matrix interactions with waste species are characterised using chromium, molybdenum, uranium and arsenic as examples. Formation of relatively insoluble precipitates, by reaction of waste species with cement components, provides chemical control over leach rates and accounts for many of the observed retentive properties.

It is concluded that further focused research is needed to characterise the future performance of cement matrices in open system environments, where chemical exchanges occur between cements and the disposal environment. © 1997 Elsevier Science B.V.

*Keywords:* Cement solidification; Cement stabilisation

---

## 1. Introduction

The use of alkaline cements for waste treatment and conditioning of liquid, semi-solid and particulate wastes for disposal has an extensively documented history and a well-established technology. Connor [1] reviews the present state of the art, including the patent literature. However, many fundamental aspects of conditioning, essential to provide a scientific basis and establish confidence in the technology, remain poorly understood and lack quantification. This presentation reviews the materials science of cement conditioning, the properties of the products, the state of fundamental knowledge concerning conditioning mechanisms and the future performance of cemented wastes.

## 2. Matrix formulations

### 2.1. Introduction

Alkaline matrices such as  $\text{Ca}(\text{OH})_2$  and Portland cement are commonly used in waste conditioning because they are inexpensive, have an extensively documented history of use and draw upon readily-accessible technology. Their alkalinity greatly reduces the solubility of many inorganic toxic or hazardous inorganics and inhibits microbiological processes. Moreover, since these matrices require water for hydration, they readily incorporate wet wastes.

### 2.2. Lime

The precursor,  $\text{CaCO}_3$ , is abundant in nature. Its thermally-decarbonated product,  $\text{CaO}$ , or lime, reacts with water to yield  $\text{Ca}(\text{OH})_2$ : or “hydrated lime”, which occurs sparingly in nature as the mineral portlandite. The hydration reaction of lime is strongly exothermic and the resulting product,  $\text{Ca}(\text{OH})_2$ , is somewhat soluble, ca.  $1.2 \text{ g l}^{-1}$  at  $18^\circ\text{C}$ , which conditions an aqueous pH of  $\approx 12.5$ . Lime may be mixed with sand, to form mortar, or with sand and coarser aggregate to form concrete: these definitions are preserved when Portland cement is substituted in whole or in part for  $\text{Ca}(\text{OH})_2$ .

In the presence of moisture and  $\text{CO}_2$ , both lime and cement matrices will recarbonate slowly although without significant dimensional change. Lime-based products are characterised by being rather porous and having poor mechanical strength.

### 2.3. Portland cement

Early in the 19th century, cements were developed which would both achieve higher compressive strengths than lime-based products and, moreover, set and gain strength in the presence of excess water. The most important, termed Portland cement on account of its resemblance to stone from that area, is now manufactured worldwide: production exceeds  $10^9$  tonnes  $\text{yr}^{-1}$ . The manufactured product is made from selected raw materials which are blended and reacted, usually in a rotary kiln, at temperatures exceeding  $1400^\circ\text{C}$ . Table 1 gives preferred ranges of chemical composition. The resulting calcined

Table 1  
Chemical composition of Portland cement

Oxide	Weight %
CaO	61–67
$\text{SiO}_2$	17–24
$\text{Al}_2\text{O}_3$	3–8
$\text{Fe}_2\text{O}_3$	1–6
MgO	0.1–4
$\text{Na}_2\text{O} + \text{K}_2\text{O}$	0.5–1.5
$\text{SO}_3$	1–3

product, termed clinker, is finely ground prior to use, normally to a specific surface of 3000–5000 cm<sup>2</sup> g<sup>-1</sup>.

Mineralogically, Portland cement clinker consists of four principal phases. These have idealised compositions close to Ca<sub>3</sub>SiO<sub>5</sub>, Ca<sub>2</sub>SiO<sub>4</sub>, Ca<sub>3</sub>Al<sub>2</sub>O<sub>6</sub> and Ca<sub>2</sub>(Al,Fe)O<sub>5</sub>. Free lime, CaO, normally comprises less than 2–3% of the clinker. Modern clinkers contain 40–60% Ca<sub>3</sub>SiO<sub>5</sub> and as a consequence the resulting finely-ground product reacts rapidly with water and stiffens. In order to allow a period of plasticity for mixing, transportation and handling, several wt% gypsum, CaSO<sub>4</sub> · 2H<sub>2</sub>O, is normally inter-ground with clinker. This retards initial set. The amount of gypsum added is usually adjusted so as to achieve retardation of initial set for several hours.

#### 2.4. Pozzolanic additives

Many materials exist, both in nature and as artificial products, which are not cementitious in their own right, but whose inherently cementitious nature can be “activated” by adding lime, Portland cement or other alkali sources. The Romans used Ca(OH)<sub>2</sub> – activated volcanic ash containing either (or both) siliceous glass and crystalline zeolite: indeed the name “pozzolan” is derived from a classic locality in Italy. The term “pozzolanic” has subsequently been extended to imply a reaction mechanism(s) rather than a specific origin or mineralogy and it is now used to embrace a range of man-made materials, principally iron blast furnace slag and coal-combustion fly ash.

The composition and mineralogy of iron blast furnace slag is relatively straightforward. Metallurgical requirements limit slag compositions to a narrow zone of the CaO–MgO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub> system: Table 2 shows typical ranges of composition. Since the glass is more active than crystalline phases, molten slag intended for pozzolanic applications is normally water-quenched to ensure a high glass content. Other types of slag are less useful and require to be evaluated to ensure that they are mainly glass and do not contain deleterious minerals or components, e.g. free MgO, which is expansive when hydrated, or which contain set inhibitors for cement, such as heavy metals, phosphates, borates, etc.

Table 2  
Composition of iron blastfurnace slag

Oxide	Weight %
CaO	36–44
SiO <sub>2</sub>	29–38
Al <sub>2</sub> O <sub>3</sub>	10–18
Fe <sub>2</sub> O <sub>3</sub>	0.2–2.0 <sup>a</sup>
MgO	4–12
Na <sub>2</sub> O + K <sub>2</sub> O	1–2
SO <sub>3</sub>	1–2.5 <sup>b</sup>

<sup>a</sup> Iron is present as Fe(II) and Fe(III).

<sup>b</sup> Sulfur overwhelmingly present as S<sup>2-</sup>.

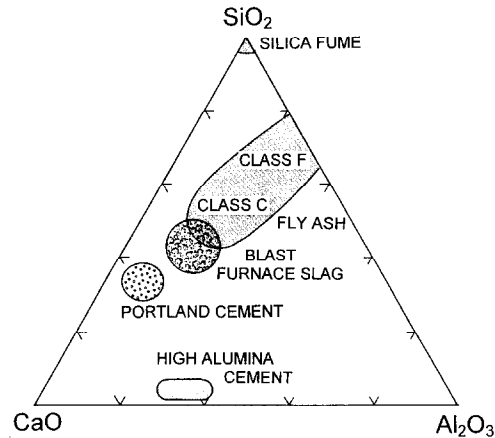


Fig. 1. The range of compositions of Portland cement and some blending agents are projected on a ternary composition grid,  $\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$ . Slag also contains significant  $\text{MgO}$ . Types F and C refer to an obsolete but persistent ASTM classification of fly ash.

Coal combustion fly ash is more complex: coals vary in accessory mineral geochemistry, with corresponding variations in ash content and composition. Fig. 1, taken from [2], indicates the wide range of compositions obtained from commercial coals. The most reactive fraction of the alumina and silica-rich ashes is glass. Typically, this glass is more siliceous and less reactive than slag glass, although the characteristically high surface area of ash particles may compensate for the diminished specific activity: Fig. 2 shows a micrograph of a representative glassy ash containing solid, bubble-like spheres, some of which are hollow and packed with still smaller spheres. The lower-silica, lime-rich fly ashes contain little glass but, on the other hand, they may contain crystalline phases which, in conjunction with an activator, react with water:  $\text{CaSO}_4$ ,  $\text{Ca}_2\text{SiO}_4$ , calcium aluminates, etc.

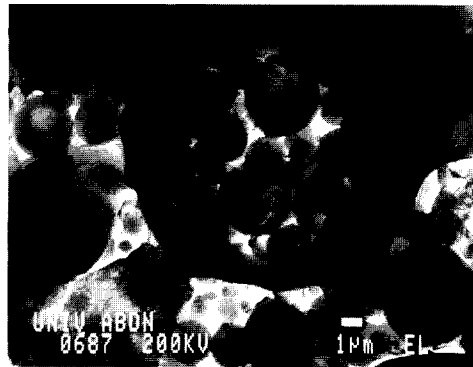


Fig. 2. Glassy spherulites of coal combustion fly ash. Note the broken sphere enclosing other spheres. The bar is  $1\ \mu\text{m}$ .

$\text{Ca}(\text{OH})_2$  and Portland cement are not the only activators for slag and fly ash. Other alkaline aqueous solutions can be used, for example NaOH, KOH,  $\text{Na}_2\text{CO}_3$  and sodium silicate or “water glass”. Alkali and calcium sulfates can also be used. Although their aqueous solutions are near-neutral, hydration reactions with slag or fly ash partially precipitate sulfate, leaving  $\text{OH}^-$  as the soluble counterion, with the result that the permeating aqueous phase rapidly becomes alkaline. Mixed activators, for example, Portland cement and calcium sulfate, are also frequently used in formulations for waste conditioning. The calcium sulfate may itself be a waste material, so a wide range of waste materials (slags, coal combustion ash, gypsum and active anhydrite, etc.) can be used as matrix formers.

Numerous other synthetic pozzolans exist. For example, the naturally-occurring mineral, kaolin, if heated to 400–700°C, partly decomposes to a nearly anhydrous phase which still preserves some of the structure of the precursor. This material, termed metakaolin, has an Al/Si ratio  $\sim 1$  and is a good pozzolan. Silica fume, derived from ferrosilicon smelters, is also pozzolanic. It arises from vapor phase oxidation of gaseous silicon; as a consequence, it is X-ray amorphous and has a very high specific surface, normally in excess of 10,000  $\text{cm}^2 \text{g}^{-1}$ . It is typically used sparingly (5–15%) in conjunction with Portland cement to formulate high strength, impermeable mixes.

### 2.5. *Water and soluble constituents*

Water is essential to initiate the hydration reactions but a broad range of water/cement ratios can be sustained. If flowable mixes are required, water/cementitious material weight ratios ( $w/c$ ) usually lie in the range 0.4–1.0. The chemical water demand for cement hydration lies close to a  $w/c$  ratio 0.25, i.e. below the lower limit for fluidity. Water in excess of the minimum required for hydration increases fluidity but also increases the porosity and ultimately, the permeability of the hardened product. Thus, if low permeability barrier materials are required,  $w/c$  ratios need to be kept as low as possible consistent with other requirements. On the other hand, it may be desirable to maximise the ratio of waste to cement and, if the waste is wet or in solution, high  $w/c$  ratios may be more economic. The upper  $w/c$  ratio is limited by incomplete set. Moreover segregation increasingly becomes a problem, and at high  $w/c$  ratios it may be necessary to add a gelling or suspending agent, e.g. sodium silicate or montmorillonite clay, to inhibit sedimentation of the cementitious components or other solids, e.g. particulate wastes. Sometimes even initially-well-mixed slurries may segregate as set occurs: this type of segregation gives rise to what is known as “bleed water”. The appearance of bleed water may be transient, in which case there may be no longer-term problem of matrix inhomogeneity. But permanent bleed water is usually undesirable, especially if it contains soluble waste components.

Components of the waste may also affect set: set accelerators are known, e.g.  $\text{CaCl}_2$ , but are generally less common and also less troublesome than those which cause retardation. Perhaps the commonest retarders are acidic substances and it may be desirable to neutralise these with base, e.g. NaOH,  $\text{Na}_2\text{CO}_3$  or  $\text{Ca}(\text{OH})_2$  prior to mixing with the cement matrix-forming components. Many common inorganic anions also retard even at low concentrations; borate and phosphate are examples. Organic sub-

stances may also retard; sugars are a notable example. Many flocculent precipitates, e.g. ferric hydroxides, also retard set.

Simple physical tests are often sufficient to check for the presence of bleed water and determine whether set retardation by components of the waste will be a problem. The Vicat test, in which the depth of penetration of a weighted needle into a pat of cement paste is measured as a function of cure time, provides an adequate guide to set times.

Normally, civil engineering codes specify pure water for mixing. This is to avoid efflorescence and reduce corrosion of embedded steel. However saline mix waters, subject to the limitations described above, may be acceptable for waste conditioning. For example, Portland cement sets well when mixed with sea water; the added salts actually accelerate set and enhance slightly the rate of strength gain relative to initially pure water.

### **3. Hydration of cement and its blends**

#### *3.1. Hydration reactions*

Because of the importance of cement to civil engineering, cement hydration has been intensively studied. Recent books review the subject in more detail than can be given here [3,4]. The chemical reactions are complex, partly because of the polyminerale nature of cement clinker and the presence of admixtures, and partly because of the complex reaction kinetics and ill-defined nature of the products obtained. However, a simple account suffices to explain the conditioning properties. Upon mixing Portland cement with water, heat is evolved and the mix water becomes strongly alkaline. However, reaction slows after a few minutes and the following period, known as the induction period, or dormant period, normally lasts several hours. The macroscopic behaviour of the system may be correlated with the microstructural changes which occur. During the first few minutes of reaction, the anhydrous clinker grains become coated with a nearly-amorphous precipitate which acts as a semi-protective film and slows reaction during the induction period. During this stage, the mix remains relatively fluid. Towards the end of the induction period, breakdown of the film marks the onset of rapid hydration. This onset also initiates the development of a continuous but initially tenuous gel network linking particles, with the result that physical stiffening occurs. Shortly thereafter, as the gel continues to stiffen and densify, strength gain commences. Typical modern Portland cements achieve about two-thirds hydration in 28 d, although some anhydrous clinker remains even after a year.

Since the overall hydration process is strongly exothermic, large, cement-rich masses may need to be proportioned so as to avoid unacceptable temperature rise. High set temperatures,  $> 55^{\circ}\text{C}$ , lead to poor strength development while consequential thermal gradients lead to thermal cracking and unequal water distribution within the set product. Generally, the larger the physical size of monoliths, the more attention has to be given to the thermal regime especially during the first few days.

The rate of cement hydration is rather insensitive to temperature in the range  $0\text{--}40^{\circ}\text{C}$ , whereas the kinetics of slag and fly ash hydration are more temperature dependent.

Table 3  
Phases present in a hydrated portland cement <sup>a</sup>

Name and/or Abbreviation	Approximate Formula <sup>a</sup>	Amount Present %
C–S–H Calcium Silicate Hydrogel	1.7CaO.SiO <sub>2</sub> .2.1H <sub>2</sub> O	50–60
Af <sub>m</sub>	Ca(OH) <sub>2</sub>	20–30
Af <sub>m</sub>	4CaO.Al <sub>2</sub> O <sub>3</sub> .SO <sub>3</sub> .12H <sub>2</sub> O <sup>b</sup>	0–10 <sup>c</sup>
Af <sub>t</sub> , Ettringite	6CaO.Al <sub>2</sub> O <sub>3</sub> .3SO <sub>3</sub> .32H <sub>2</sub> O <sup>b</sup>	0–10 <sup>c</sup>

<sup>a</sup> Hydration assumed occur at 0–30°C.

<sup>b</sup> May contain some Fe in place of Al: in AF<sub>m</sub>, substitution of 2 OH for SO<sub>4</sub> may also occur.

<sup>c</sup> Sulphate content of cement affects the balance between AF<sub>m</sub> and AF<sub>t</sub> phases.

Although slags are generally said to hydrate more slowly than cement, warm, cement-activated blends hydrate rapidly with approximately the same heat liberation as cement at temperatures above 60°C. Since slag is frequently added with the intent of reducing the thermal excursion during hardening, it is obvious that the conditions of heat flow, and hence temperature rise, need to be taken into account to predict whether this strategy is appropriate.

The kinetics of slag and fly ash hydration are difficult to measure directly: engineers tend to use indirect measures, such as compressive strength development. But strength development is a complex function of many factors, including the clinker mineralogy, grain packing and water content, as well as extent of reaction. Taylor [5] finds that the rate of hydration of slag at constant temperature is linear as a function of time whereas others have found a definite plateau, during which little chemical reaction occurs [6]. While strength gain is often not a primary concern in waste conditioning, unreacted particles—cement, fly ash, slag—behave as inert fillers and it may be advantageous to ensure that the chemical conditioning action of the matrix is optimised by achieving a high degree of hydration of all the cementitious components.

The products of hydration of Portland cement include both crystalline and amorphous phases. Table 3 summarises the composition and properties of these phases. The microstructure of a typical, well-made Portland cement paste (w/c ratio 0.4) is shown in Fig. 3. Just as the mineralogy defines the chemical properties of the system, the microstructure defines its physical properties (permeation, percolation). In Fig. 3, the main crystalline phases, Ca(OH)<sub>2</sub> and ettringite, appear as plates or columnar crystals and rods or needles, respectively. The monosulfoaluminate phase, known to be present by X-ray, often has less well-developed morphology and tends to be occluded within the bulk of the gel phase. This gel phase, designated C–S–H (cement shorthand: C = CaO, S = SiO<sub>2</sub>, H = H<sub>2</sub>O) has a Ca/Si ratio between 1.8 and 2.0 although, in blended cements, its C/S ratio may decrease to as low as 0.9: the impact of blending agents on cement mineralogy will be described subsequently. The gel is typically massive and rather featureless at the micrometer scale. Nevertheless, it is the principal constituent of Portland cement and on account of sorption within its nanoporosity, it controls many of its sorptive properties associated with hydrated cements. From Fig. 3, it can be appreciated that the microstructure is complex. Direct measurement of pore sizes is not

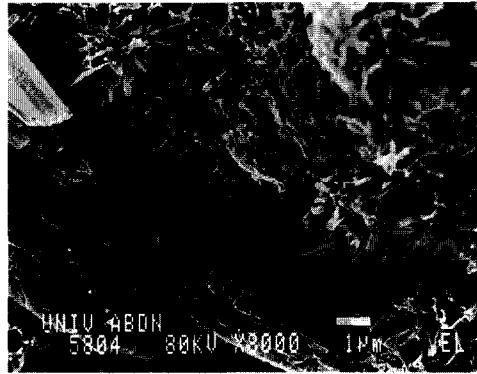


Fig. 3. Microstructure of a hardened Portland cement. The fracture discloses large plate-like and blocky crystals of  $\text{Ca}(\text{OH})_2$ , frequently associated with pores. These pores are normally water-filled, but water evaporates in the high vacuum of the electron microscope. The smaller, lath-like crystals are hydrated calcium sulfoaluminates. The bulk of the matrix is an inorganic gel. Spherulitic growths of this gel occupy space formerly filled by cement clinker grains. The bar is 1  $\mu\text{m}$ .

practicable and it has proven difficult to quantify the microstructure, not least because its features range from nanometer to sub-millimeter scale.

### 3.2. Porosity–permeability relations

Cements are intrinsically porous materials. In the high vacuum of the electron microscope the pores dry out and appear empty, or nearly so, but in bulk paste they are normally filled with fluid. Pore water expression, using a high pressure, enables the pore fluid to be sampled directly while complimentary techniques, e.g. mercury intrusion porosimetry and gas sorption isotherms, enable the pore volume and size distribution of dried pastes to be measured. The paste also contains a broad spectrum of pore sizes: the intrinsic nanometer-scale pores of C–S–H have been noted. Incomplete filling of space between former clinker grains by their hydration products creates mesopores, typically in the range 0.05–1  $\mu\text{m}$ , and entrapped air or gas contributes to the macroporosity above approximately 1  $\mu\text{m}$ . Table 4 summarises the characteristic pore regime of paste. However if larger particles, e.g. sand grains or particulate wastes, are embedded in paste the interface between paste and particles frequently comprises a zone of poor packing, with the result that interfaces also contribute to the overall mesoporosity. Moreover,

Table 4  
Pore size regime in hydrated cement paste

Characteristic size	Origin and physical significance
Nanometer	Intrinsic feature of C–S–H gel ultrastructure
Submicron	Excess water not required for chemical hydration
Micron to millimeter	Air bubbles, poor packing at paste–particle interfaces



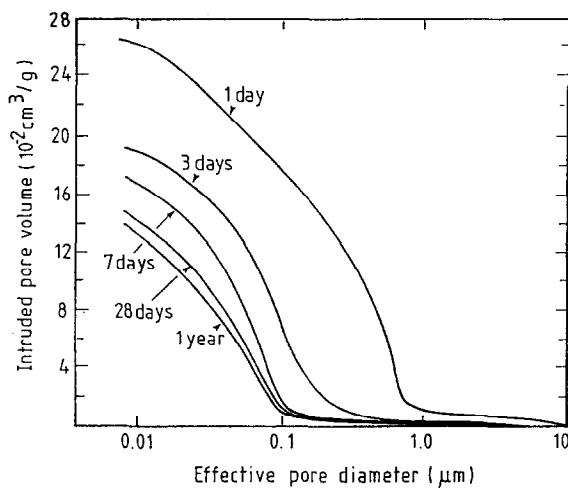


Fig. 4. Mercury intrusion porosity scans, showing the decrease in pore size and the shift to smaller pore entry diameter as cure progresses. The paste was made to a w/c ratio of 0.36 and cured at 22°C.

local concentrations of mesopores at interfaces form permeable zones. This explains the apparent paradox that, while a low w/c ratio paste may have a permeability  $\approx 10^{-12} \text{ ms}^{-1}$ , mortars formulated with the same cement and impermeable sand typically have much greater permeabilities. Thus it is easier to characterise intrinsic paste properties than those of mortars where complex interface reactions also occur.

The total porosity of a paste system typically lies in the range 16–24%. Mercury intrusion scans, Fig. 4, show how the mesoporosity evolves as cure progresses. The intrinsic, nanometer scale gel porosity is too small to be revealed by mercury intrusion, but can be determined by gas sorption or by neutron scattering.

The introduction of fly ash and slag do not much affect the total paste porosity, other factors being equal, but they do reduce pore connectivity with the result that well-cured blends may achieve low permeabilities,  $< 10^{-12} \text{ ms}^{-1}$ . This process, termed pore refinement, has been explored by a wide range of methods [7]. The pore refinement in cement and its blends occurs relatively slowly: with good curing, porosity and permeability decrease steadily over the first 6–12 months: perhaps even beyond.

From this presentation, it can be appreciated that the exact relationships between porosity, permeability and diffusion are complex. Percolation theory has usefully been applied to cements and it discloses that particulate systems tend to have a critical porosity threshold which, when exceeded, leads to a rapid increase in permeability [8]. These considerations are important in the design of cementitious compositions intended as physical barriers. However ideal physical barrier performance may be difficult to achieve in real, large-scale applications: not only are low water/cement ratios required but cements are intrinsically brittle materials and, as such, are subject to cracking. Physical cracks define short-circuit transport paths. Thus cracking has also to be considered in treatments of physical barrier action. Cracking is, however, of less significance to the chemical aspects of immobilisation.

### 3.3. Pore water

The pore water, it will be recalled, is the excess of aqueous phase which is not required for hydration. As the matrix hardens, mix water gradually diminishes in amount and at some point, usually defined operationally as the final set time, the remaining aqueous phase becomes sufficiently discontinuous to permit its description as pore water. Although cements may contain relatively little  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$ —perhaps only 0.5–1.0 wt %—the alkali concentrates in pore water. Since anions other than  $\text{OH}^-$  are relatively insoluble, cement alkalis are effectively present as  $\text{NaOH}$  and  $\text{KOH}$ , with the result that they dominate the pore fluid alkalinity. The pore fluid pH frequently exceeds that of saturated  $\text{Ca}(\text{OH})_2$  ( $\approx 12.4$  at  $18^\circ\text{C}$ ), reaching 13 to 14. The exact value depends on cement alkali content, alkali availability for solution, the water/cement ratio and the content of added alkali in activators, amounts of mix water and waste and the presence of soluble waste components. But the cement will not set except at high pH. The most immediate consequence of the very high internal pH is that the high hydroxyl concentration suppresses the solubility of Ca. However, solid  $\text{Ca}(\text{OH})_2$  and other lime-rich solids combine with waste components and remain to buffer the pH, should alkalis be leached. Thus the importance of pore water is two-fold; first, it conditions rapid reactions between waste components and cement and second, its interconnectivity dominates matrix diffusion characteristics.

### 3.4. Impact of blending agents

In normal civil engineering practice, up to 30–40% of cement may be substituted by fly ash and up to 65–70% by blast furnace slag: waste conditioning technologies may utilise even higher replacement levels. Needless to say, major additions of reactive fly ash or slag will affect the mineralogy of the hydrate products. This may not be immediately apparent since, in the short term, the chemical properties of the system are dominated by the more rapid hydration reactions of the cement component. But slag and fly ash will eventually react and, in the course of reaction, will affect the mineralogy and other system properties, including pore fluid compositions. One important consequence of reaction is the reduction and even elimination of free  $\text{Ca}(\text{OH})_2$  by reaction with slag and fly ash, both of which are more silica-rich than cement. The reaction is akin to an acid-base reaction: alkaline  $\text{Ca}(\text{OH})_2$  reacts with the more “acidic” silicate components. However, the principal reaction product, C–S–H, is itself sufficiently soluble to condition a relatively high pore fluid pH, ranging from  $\approx 12.5$  for high calcium C–S–H to ca. 10.5 for low lime C–S–H (Ca/Si 1.0). It should be noted that these pH values are conditioned by the intrinsic solubility of the phase or phase mixture and, in general, do not depend on the amounts of the phase(s). But as the Ca:Si ratio of the gel decreases, its sorption of cations—especially Na—increases. Thus, blended cements may have higher total alkali contents than Portland cement yet exhibit lower pore fluid pH values as a consequence of greater alkali uptake into solids.

Much literature focuses on the formation of minor hydrate products: for example, Al from fly ash forms “gehlenite hydrate”,  $2\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2 \cdot 8\text{H}_2\text{O}$ , while Mg from slag forms phases closely related to the natural-occurring mineral hydroxycalcite. But while

these phases may potentially have interesting specific sorptive properties, they generally remain minor phases relative to C–S–H. Thus the calcium silicate gel is the principal conditioning phase throughout a broad spectrum of cement and blended cement compositions. In common with many other inorganic gels, its “structure” is not well known, although specific attributes are well characterised: for example, its nanoporosity.

#### 4. Source of the immobilisation potential

##### 4.1. Chemical and physical mechanisms

The distinction between the purely chemical and purely physical mechanisms is not always clear-cut. Scale is important in making a distinction: chemical immobilisation characteristically occurs at an atomic scale, whereas physical immobilisation occurs over longer distances, for example on a micron scale. An example occurs when a floc or fine-grained precipitate is dispersed in a cementitious matrix, or on a larger scale, perhaps up to metre scale, in physical barrier walls or grout curtains. In many applications, however, chemical and physical mechanisms operate conjointly and it is impractical to make clear-cut distinctions. Many other waste matrix-forming materials, e.g. organic polymers and bitumen, lack significant chemical fixation, the presence of which is thus a distinctive and important potential advantage of cementitious systems. But the chemical conditioning action is perhaps the least well understood aspect of cement performance and I concentrate on defining this potential by means of selected examples.

##### 4.2. Internal chemical state

Despite the apparent solidity of cement matrices, chemical concepts applicable to aqueous solutions, e.g. pH, are useful characterisation parameters because of the presence of pore fluid. Table 5 shows the chemical make-up of pore fluid and the reservoirs of solid which are potentially available to react with wastes. In most cases, the aqueous reservoirs are buffered by solids. In the following discussion, the boundary between “soluble” and “insoluble” components will be arbitrarily fixed in the range 1–10 ppm. In general, alkalis are the most soluble constituents. Indeed, in many conservative estimates of cement performance, it is assumed that they will be leached relatively early in the history of the disposal site, leaving  $\text{Ca}(\text{OH})_2$  or C–S–H gel, or

Table 5  
Major aqueous and solid components in cement

Aqueous components	$\text{Na}^+$ , $\text{K}^+$ , $\text{Ca}^{2+}$ , $\text{OH}^-$ , $\text{SO}_4^{2-}$
Solid components of:	
cement	Ca, Al, Fe, Si
fly ash	Al, Si
slag	Ca, Al, Si, Mg, $\text{S}^{2-}$

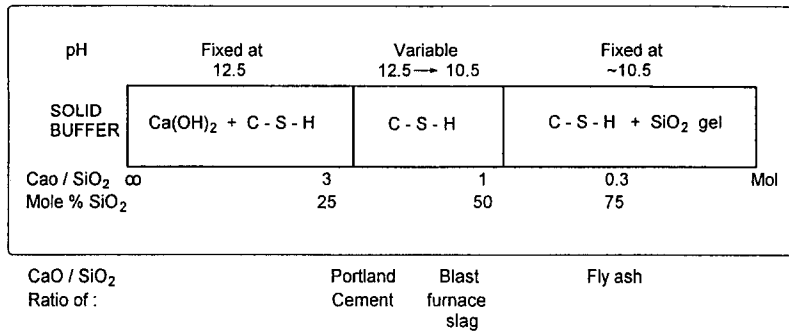


Fig. 5. The pH developed by CaO–SiO<sub>2</sub>–H<sub>2</sub>O cement phases in contact with aqueous solutions at 20°C.

both, to buffer the aqueous pH. Fig. 5 shows the dependence of aqueous pH on the nature of the calcium silicate buffers. The composition of Portland cement, slag and fly ash are indicated very approximately in Fig. 5; fully reacted blends with Portland cement project at intermediate positions, depending on the blend proportions. Chemical models of this behaviour are well supported by experimental evidence [9,10] on the aqueous reactions of the calcium silicate buffers. The composition of Portland cement, slag and fly ash are also indicated very approximately in Fig. 5; fully reacted blends with Portland cement project at intermediate positions, depending on the blend proportions.

Another aspect of cement behaviour is the oxidation-reduction potential they impress on the aqueous phase and hence on waste components. Portland cements are normally produced under oxidising conditions; thus most of their iron content is present as Fe(III), to the near-exclusion of Fe(II). Not surprisingly, therefore, its associated pore fluids are slightly oxidising, having potentials relative to a standard hydrogen electrode of +100 to +200 mV. However, both lime-based and Portland cements lack any active redox couples, so the numerical value of the redox potential, or  $E_h$ , is readily affected by the presence of active redox couples. These active couples may be furnished by blending agents, by waste constituents, or both. The most  $E_h$ -active blending agent is iron blast furnace slag. Slags contain a little iron which is present as mixtures of colloidal metallic iron, Fe(II) and Fe(III). The main couples involve sulfur. S<sup>2-</sup> substitutes in part for O<sup>2-</sup> in the glass network. This chemically-reduced S reacts with water at high pH and with cement sulfates to furnish a range of electrochemically active S speciations: S<sup>2-</sup>, S<sub>x</sub><sup>2-</sup>, S<sub>2</sub>O<sub>3</sub><sup>2-</sup>, SO<sub>3</sub><sup>2-</sup> and SO<sub>4</sub><sup>2-</sup>. Slag-rich blends have been experimentally observed to have  $E_h$  values in the range –200 to –400 mV and, moreover, to have better poisoning capacity than cements since much of the sulfur is retained in solids [11].

Against this background specific reactions of waste species with free water at high pH and a range of  $E_h$  values can be analysed (Table 6).

#### 4.3. Reactions between cement and waste components

##### 4.3.1. General considerations

The reactions between cement and waste components is complex and have been only partially systematised. Fig. 6 and Table 6 summarise these reactions. It is possible,

Table 6  
Reaction and controls on species solubility

Factor	Methods of control
Species oxidation state	Reduce anionic forms (more soluble) to less-soluble cationic forms by pretreatment with ferrous salts, iron metal, etc. Condition low $E_h$ with blast furnace slag, etc.
Species solubility as hydroxide or hydrous oxide	Use $\text{Ca}(\text{OH})_2$ or Portland cement to condition $\text{pH} \approx 12.5$ . Avoid if possible excess of (Na,K) which may give $\text{pH} > 12.5$
Species solubility as complex salt	Ca activity normally high but adjust availability of other cationic, (e.g. Mg) and anionic species, (e.g. Al, $\text{SiO}_4$ , $\text{SO}_4$ , $\text{CO}_3$ ), as required

within limits imposed by the stability of water, to control species oxidation state. This control is frequently employed in conditioning: for example, Cr(VI) is readily reduced to its (III) state by pretreating liquid wastes with ferrous sulfate, since Cr in its (III) state is more successfully insolubilised in cement matrices. The same result can be achieved, albeit more slowly, as for example by using iron blast furnace slag as part of the cementitious material. However, it is useful to demonstrate how, in general, system properties influence toxic element solubility.

#### 4.3.2. pH

The alkaline solution chemistry of inorganic species enables three classes of behaviour to be defined: species may be soluble in alkaline conditions, insoluble or amphoteric. The species which escape precipitation are characteristic of the first class. The intermediate, amphoteric, class are relatively insoluble at near-neutral pH but become increasingly soluble as the pH increases. Of course, the distinction between different classes is somewhat arbitrary: there are few inorganic species which do not exhibit at least partial amphoteric character at extremely high pH,  $\geq 14$ . Of primary concern here are pH's in the range 11–13, in which an elemental classification usefully anticipates behaviour in cement useful descriptor. Fig. 6, after [11], shows a classification of the elements. Since speciation is much affected by oxidation state, the figure depicts the species stable at  $E_h$  values of +200 mV or less in alkaline pH.

#### 4.3.3. pH- $E_h$ relations

Another method of depicting speciation and solubilities of specific elements is by means of the Pourbaix diagram. Fig. 7, taken from the Pourbaix atlas [12], shows the diagram for Cr on which pH- $E_h$  regimes characteristic of cement and well-cured slag blends are superimposed. It can be seen that Portland cements lie close to the Cr(III)–Cr(VI) boundary and indeed, the initial oxidation state of Cr in Portland cements tends to be indifferent to its initial oxidation state. Thus, in the absence of other factors, Cr(VI) and Cr(III) both persist. However, Cr(VI) is readily reduced to (III), whereas the reverse is more difficult to achieve.

Practical experience suggests that Cr(III) is much better immobilised than Cr(VI). Yet the reasons for this are not immediately apparent. Cr(VI) is very soluble in alkaline

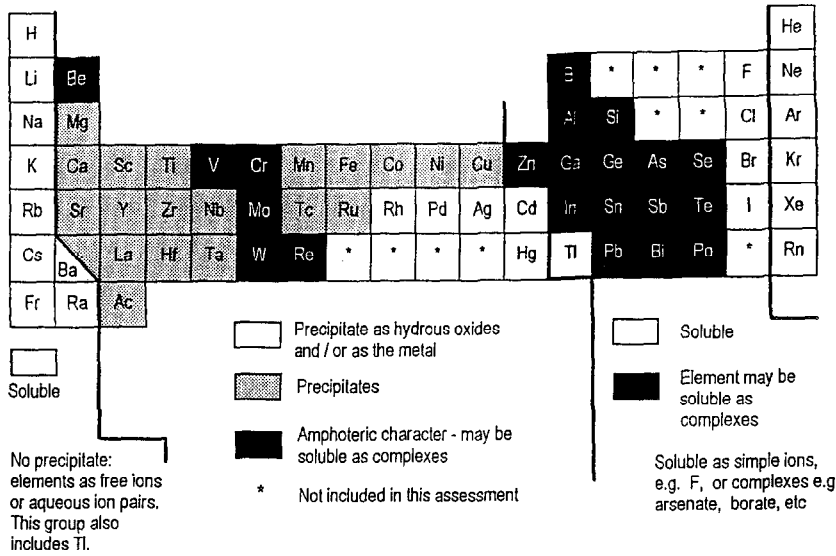


Fig. 6. Schematic classification of the behaviour of aqueous species (the most common oxidation state is assumed) towards cement-conditioned water.

solutions but so too is Cr(III). Thus, if it is supposed that Cr(III) is precipitated as Cr(OH)<sub>3</sub>, its solubility at pH 12.5 is several orders of magnitude greater than values obtained from in pore fluids.

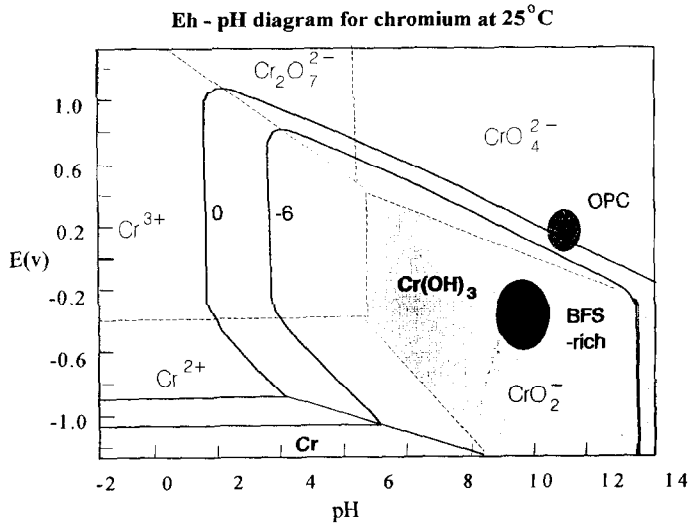


Fig. 7. Pourbaix diagram, showing the principal aqueous speciation of chromium as a function of oxidation-reduction potential,  $E_h$ , and pH at  $\approx 20^\circ\text{C}$ . The  $E_h$  is relative to a standard hydrogen electrode. Regimes characteristic of the internal environments of OPC and OPC/slag blends are shown by dark regions.

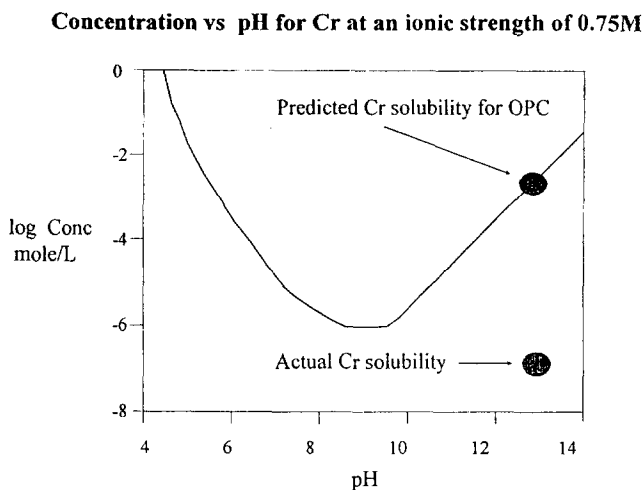


Fig. 8. Solubility curve calculated for  $\text{Cr}(\text{OH})_3$  as a function of pH. The actual solubility of Cr in cement-conditioned water at  $\text{pH} \approx 12.5$  lies in the range 0.1–1.0 ppm, several orders of magnitude less than the solubility of  $\text{Cr}(\text{OH})_3$  at the same pH (circles). See text for discussion.

Fig. 8 contrasts observed Cr solubility in cements with simple predictions based on  $\text{Cr}(\text{OH})_3$ . From this model the high pH of cements would appear to lie well beyond the point of minimum solubility and cements would not be expected to comprise a very satisfactory chemical matrix for binding Cr(III). But the actual measured solubility of Cr(III) in the pore fluid of a matured Portland cement lies several orders of magnitude below the predicted value. This discrepancy arises because the hypothesis used as the basis for calculation is too simplistic. Cement hydration products contain octahedrally coordinated Al, which is readily replaced by Cr(III). Thus, the chemical immobilisation potential is due to formation of calcium aluminate hydrate phase(s), in which Al is partly replaced by Cr(III). Thus while Cr(III), like Al, is amphoteric, both remain relatively insoluble in the cement environment. In conclusion, just as the solubility of Al at pH 11–13 is controlled by the solubility of calcium aluminate hydrates and not by  $\text{Al}(\text{OH})_3$ , so the solubility of Cr(III) is limited by the solubility of calcium (chromium (III)-aluminium) hydrates. Since these have negative free energies of formation with respect to mixtures of  $\text{Ca}(\text{OH})_2$ ,  $\text{Cr}(\text{OH})_3$ ,  $\text{Al}(\text{OH})_3$  (or/and  $\text{Cr}(\text{OH})_3$  and water, Cr(III) solubility is greatly decreased with respect to simplistic models based on the solubility of  $\text{Cr}(\text{OH})_3$ . Reaction may not be rapid; initially, Cr may partly precipitate as  $\text{Cr}(\text{OH})_3$ , and the true solubility-limiting phase may require weeks or months to form, during which the pore fluid Cr solubility decreases to a steady-state value in the range 0.1–1.0 ppm.

The state of knowledge concerning reactions between cement and waste species is very variable. Moreover, it is not always possible to generalise from position in the periodic table, by extending the behaviour of one element to others of the same group. For example, Table 7 summarises data for the Cr, Mo, U group. Unlike Cr, Mo cannot readily be reduced in cement pore fluids. However, the high lattice energy of powellite,  $\text{CaMoO}_4$ , allows it to precipitate at high pH with the result that the solubility of Mo(VI)

Table 7  
Reactions of the Cr, Mo, U group with cement

Element	Species M(III)	Stability M(VI)	Characteristics. Solubility-limiting phase(s)
Cr		Yes	Poorly immobilised, substitutes for $\text{SO}_4^{2-}$ to a limited extent
Cr	Yes		Forms calcium (chromium III, aluminium III) hydrates
Mo	No	Yes	Insoluble $\text{CaMoO}_4$ and Mo analogues of sulfate salts
W	No	Yes	No data
U	No	Yes	Complex: calcium uranate hydrates, $\text{CaUO}_4 \cdot x\text{H}_2\text{O}$ and calcium uranyl silicates, e.g. uranophane

is very much less than that of Cr(VI). Moreover, if alumina is present, calcium aluminate molybdate hydrates also precipitate and compete with powellite as the solubility-limiting phase [13].

Uranium is more complex. The (VI) state appears to persist over a wide range of redox conditions. In silica-poor mixes, a hydrous version of  $\text{CaUO}_4$  appears to be the solubility-limiting phase. But in the presence of silica, complex calcium uranium silicates form. At least one of these phases is isostructural with the mineral uranophane; the other synthetics may also have natural analogues. These calcium uranium silicates form only slowly so, experimentally, U(VI) solubilities in cement conditioned solutions continue to decline over several years as the silicate-containing phases develop. After 2 years, U(VI) solubilities in mixes containing C–S–H gel are on the order of  $10^{-9}$  M. Uranium also has a (IV) state which may be stable in cements. Its behaviour is still being studied, but, like Th(IV), Zr(IV) and Hf(IV), it is believed to be very insoluble. A number of naturally occurring, low-solubility minerals containing both (IV) and (VI) states are known and these may serve as models for the behaviour of mixed-valent U in cement.

This brief review highlights those elements where the solubility limiting phase is known. But for many elements, the solubility controls are not known. Consequently, it is difficult to anticipate what performance can be expected from cement systems. Fig. 9

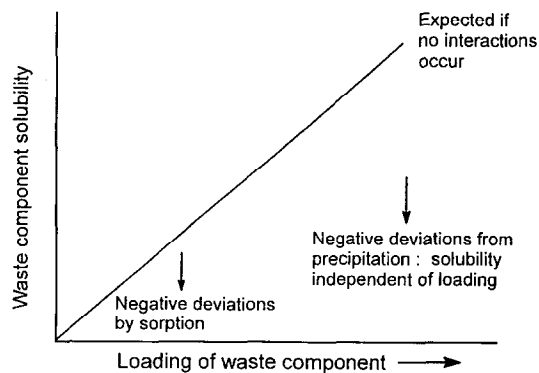


Fig. 9. Schematic diagram of the interactions between cement and a waste species as a function of loading. Many species exhibit characteristic sorption at low concentration, with one or more plateaus, resulting from discrete phase formation, occurring at higher species concentrations.



shows schematically how mechanism relates to solubility of the toxic species. For a wide range of solubilities, both physical and chemical controls are important. However, the diagram cannot be quantified because scale effects are important for physical controls, whereas they are less important for chemical conditioning controls.

#### 4.3.4. Leach studies

Leach tests are widely used as indicators of matrix performance. However, leach test data on cementitious components do not generally enable a distinction to be made between physical and chemical mechanisms although, other factors being equal, the order of leachability is generally a good qualitative guide to the presence or absence of specific chemical binding mechanisms. Empirical experience suggests that most cationic electropositive elements with formal charge of III or more are well-insolubilised in cement matrices by specific chemical mechanisms. Anionic speciations are, however, less well bound; examples include the semi-metals/metals of the *p*-block. Thus, As occurring as  $\text{AsO}_3^{2-}$  or  $\text{AsO}_4^{2-}$ , (As(III) and (V), respectively), is not well bound. Some arsenate,  $\text{AsO}_4^{2-}$ , will substitute for the sulfate phases of cement hydration products but partition coefficients between aqueous and solid phases do not indicate good binding for large, tetrahedral species. This is most pronounced for species having the structure  $\text{MO}_3$ : (where: corresponds to an electron pair occupying a tetrahedral vertex). Thus  $\text{AsO}_4^{2-}$ , arsenate, is somewhat better fixed than  $\text{AsO}_3^{2-}$ , arsenite.

In general, the occurrence of solubility limiting phases at low concentration results in an overall solubility pattern similar to that shown in Fig. 9. At extremely low concentrations, below the threshold for precipitation, solubilities tend to be controlled by sorption mechanisms. C–S–H, with its high specific surface area and range of sorption sites, is usually the main source of the sorption potential. At high C/S ratios, C–S–H has a positive surface charge and thus sorbs mainly anionic species. Since anions are abundant in cement, where the main components contribute ( $\text{OH}^-$ ,  $\text{SO}_4^{2-}$ , etc.), the performance of cements for trace toxic anions is generally poor: they have to compete with more abundant  $\text{OH}^-$  etc. for anionic sites. However, as the surface charge becomes positive, as occurs at low Ca/Si ratios, the more siliceous C–S–H's exhibit improved sorption for cations. But all C–S–H's, irrespective of Ca/Si ratio, have a range of sorption sites, so that cations are never sorbed to the exclusion of anions, and vice versa.

## 5. Ageing and environmentally-conditioned reactions

### 5.1. System behaviour

Once wastes have been cement conditioned and disposed, usually into the natural environment, further reactions may occur. Dry environments are of course favourable for containment: contact with flowing ground water constitutes a realistic worst case scenario. Two types of reaction between cement-conditioned waste and their disposal environment can therefore be envisaged, one characterised by closed system behaviour and the other, by open system behaviour. In closed systems, no reaction involving transport of matter occurs in or out of the system, whereas open systems are charac-

terised by mass transport. Both are realistic possibilities, as is shown by natural analogues of cement systems. At one extreme, they may approximate closely to closed system behaviour over long periods: hydrated calcium silicates have been observed to persist for  $> 10^6$  years. Semi-artificial examples are also known: the persistence of calcium silicate hydrates in mortars of Hadrian's Wall and in other man-made structures of comparable antiquity (ca 1800 years) are examples.

The cement matrix may, however, react with waste constituents. Degradation of organic materials could lead to formation of  $\text{CO}_2$  (or  $\text{CO}_3^{2-}$ ). The consequential reaction, carbonation of the cement, leads to loss of high pH and potential resolubilisation of waste species. Generation of "inert" gases, e.g.  $\text{CH}_4$ ,  $\text{H}_2$ ,  $\text{O}_2$ , etc. could lead to cracking and physical deterioration of the matrix. These and other mechanisms have been suggested to occur but there is little hard evidence that they will be important in practice. The most frequently cited reason for formation of  $\text{CO}_2$  and  $\text{CH}_4$  is as a consequence of microbiological action upon organic wastes. Yet the high pH of the matrix is also known to discourage microbiological activity. The relative importance of gas generation arising from decomposition of the organic components of waste streams is, by and large, unresolved. Moreover, many hazardous species form poorly soluble carbonates. These are all factors which require further research.

### 5.2. Open system behaviour

The most important reactions encountered in open systems is reaction with groundwater and its components. Straightforward leaching by initially pure water remains a possibility, although in practice, even low levels of dissolved matter present in groundwater are likely to prove important. Sensitivity studies disclose that the important groundwater components are Na, Ca, Mg (cations) and Cl,  $\text{CO}_3$  and  $\text{SO}_4$  (anions). Given the complexity of the system (cement, waste and groundwater), empirical studies of the impact of groundwater have tended to be site specific. This is especially so as groundwater constituents—especially anions—may also affect waste constituent solubilities by complexation.

Much empirical experience can be applied to predict the general reaction(s) and consequence(s) of specific groundwater components. Table 8 gives selected examples. Empirical experience needs to be quantified; laboratory studies may be required.

From the regulatory standpoint, as well as public acceptance of a safety case, leach

Table 8  
Reactions of groundwater components with cement

	Characteristic reaction
Cations	
Na, K, Ca	Very slight
Mg	Replaces Ca in $\text{Ca}(\text{OH})_2$ , C–S–H, etc. with decrease in pH
Anions	
Cl	Partially replaces OH in cement phases. Consequences slight at low $\text{Cl}^-$ concentrations
$\text{SO}_4$	Increases stability of solid sulfates. Reaction may be expansive
$\text{CO}_3$	Converts cement phases to $\text{CaCO}_3$ with decrease in pH

tests are virtually obligatory. Yet the conditions of the test are often quite unrealistic of the disposal conditions, and it is uncertain how laboratory scale experiments should be scaled up to provide an adequate guide to future performance. Accelerated tests characteristically use (i) elevated temperatures, (ii) high specific surface areas perhaps achieved by crushing or grinding the matrix and (iii) acidification of the leachant, either continuously or intermittently and (iv) frequent renewal of leachant. Perhaps the most acceptable of these accelerations is renewal of leachant: it corresponds to a disposal environment in which groundwater circulates rapidly over or percolates through the conditioned waste. The other conditions employed may or may not be realistic. For example, acidification of leachant amounts to an acid-base titration in which the matrix furnishes the base. The equilibrium is never in doubt, but the kinetics differ depending upon the acid used. Singly ionised acids, e.g.  $\text{HNO}_3$ ,  $\text{HCl}$ , mainly dissolve the matrix leaving little solid residue ( $\text{SiO}_2$  tends to remain insoluble). Doubly ionisable acids, e.g.  $\text{H}_2\text{SO}_4$ , exhibit more complex behaviour; while the cement surface layers dissolve, precipitation may also occur within the matrix, leading to pore blocking by gypsum, ettringite, etc. Thus the kinetics of dissolution are often complex and scale-dependent: powdered samples, unlike monoliths, will not generally develop mineralogical zonation. It may also be noted that the development of mineralogical zonation with precipitation does not always lead to pore blocking, with concomitant decrease in leach rates. Some precipitation mechanisms cause expansion, with the result that attack proceeds by cracking and spallation with progressive increases in surface area:volume ratio. The effects of increasing temperature are also complex: partial crystallisation of the gel matrix may occur with reduction in its specific surface area, and hence loss of sorption potential and decrease in pH.

A common fault of accelerated tests is that, by their nature, they normally allow only a brief cure duration prior to commencement of the test. During the early stages of the test, waste components may still be undergoing reactions with the matrix, leading to decreasing solubility. The occurrence of competing reactions in the course of the test do not provide a firm basis for extrapolation of data into the future.

It should be noted that many leach tests are derived from those developed for the corrosion of materials which do not significantly alter the leachant composition or affect the pH of the leachant. For example, the common corrosion products of steel are highly insoluble over a wide range of pH range and do not therefore affect pH. Cements, with their greater activity, do affect leachant pH, so many iso-pH test methods are not readily applicable, or are realistically applicable with difficulty, to cements. Thus much further work is required to develop satisfactory leach tests with predictive capabilities.

Organic complexants may also influence the solubilisation of waste species. Relatively little systematic work has been done on the subject. However, preliminary indications are that the problem may not be as severe as is sometimes supposed. Table 9 shows a few examples. Many organics are precipitated in the cement environment, e.g. oxalate as its Ca salt, so high aqueous concentrations cannot be realistically achieved [14]. Others, e.g. citrate, are destroyed. The long term consequences of  $\text{CO}_2$  production: also, of cellulose degradation products, still requires to be assessed with respect to impact on heavy metal stabilisation and solubilisation mechanisms but straightforward reduction of cement pH appears to be the most immediate problem.

Table 9  
Reactions between cement and selected organics

Type of organic	Reaction with cement
High M.W. soluble dispersible polymers, e.g. plasticisers	Hydrolysis of functional groups and irreversible precipitation
High M.W. insoluble polymers, e.g. cellulose	Possible development of lower molecular weight soluble products. Products variable depending on presence or absence of oxygen
Microbiological degradation of natural and synthetic polymers, etc.	Possible production of CO <sub>2</sub> , CH <sub>4</sub> (reducing conditions) or organic acids (oxidising conditions)
Low molecular weight complexants, e.g. citric acid, oxalic acid EDTA	Probably destroyed or precipitated, with solubility controls, at high cement pH

Many of these complex reactions would appear to be suited for modelling by computer. Indeed, this is so. Geochemists have developed the necessary routines which are widely available. Problems may arise initially because of the inadequate data base relevant to cements which are necessary to support calculations. While the prospect of rapid calculations of equilibria in complex systems is attractive, obtaining the underlying data base is less attractive. Therefore, the data base is being improved only slowly [15]. There are, nevertheless, grounds for optimism. A foundation of immobilisation science is being built, albeit slowly. The necessary computer routines are becoming available and, with expert help, are being used successfully to assess the present and future performance of cement-based systems.

## References

- [1] J.R. Connor, *Chemical Fixation Solidification of Hazardous Wastes*, Van Nostrand–Reinhold, New York, 1990.
- [2] F.P. Glasser, S. Diamond and D. Roy, *Hydration Reactions in Cement Paste Incorporating Fly Ash and Other Pozzolanic Materials*. Proc., Vol. 86, Materials Research Soc., Pittsburgh, PA, 1987, pp. 39–158.
- [3] H.F.W. Taylor, *Cement Chemistry*, Academic Press, London, 1990.
- [4] G. Frohnsdorff (Ed.), *Blended Cements*, Special Technical Publication 897, ASTM, Philadelphia, PA, 1986.
- [5] H.F.W. Taylor, K.H. Mohan and G.K. Moir, *J. Am. Ceram. Soc.*, 68 (1985) 685.
- [6] K. Luke and F.P. Glasser, *Cement Concr. Res.*, 17 (1987) 273.
- [7] R.D. Hooton, in G. Frohnsdorff (Ed.), *Blended Cements*, Special Technical Publication 897, ASTM, Philadelphia, PA, 1986, pp. 128–143.
- [8] E.J. Garboczi and D. Bentz, *Mater. Res. Soc. Bull.*, 18(3) (1993) 50.
- [9] D.E. Macphee, K. Luke, F.P. Glasser and E.E. Lachowski, *J. Am. Ceram. Soc.*, 72(4) (1989) 646.
- [10] D.E. Macphee, E.E. Lachowski and F.P. Glasser, *J. Am. Ceram. Soc.*, 70(7) (1987) 481.
- [11] D.E. Macphee and F.P. Glasser, *Mater. Res. Bull.*, 18(3) (1993) 66.
- [12] M. Pourbaix, *Atlas of Electrochemical Equilibria in Aqueous Solutions*, Pergamon Press, Oxford, 1966.
- [13] E.E. Lachowski, A.K. Minocha and F.P. Glasser, *Waste Mgmt*, 14(2) (1994) 1.
- [14] S. Smillie, M.Sc. Thesis, University of Aberdeen (in preparation).
- [15] M. Atkins, F.P. Glasser and A. Kindness, *Cement Concr. Res.*, 22 (1992) 241.