CEMENTS IN RADIOACTIVE WASTE DISPOSAL

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Abstract

The use of cement and concrete to immobilise radioactive waste is complicated by the wide- ranging nature of inorganic cementing agents available as well as the range of service environments in which cement is used and the different functions expected of cement. For example, Portland cement based concretes are widely used as structural materials for construction of vaults and tunnels. These constructions may experience a long pre-closure performance lifetime during which they are required to protect against collapse and ingress of water: strength and impermeability are key desirable characteristics. On the other hand, cement and concrete may be used to form backfills, ranging in permeability. Permeable formulations allow gas readily to escape, while impermeable barriers retard radionuclide transport and reduce access of ground water to the waste. A key feature of cements is that, while fresh, they pass through a fluid phase and can be formed into any shape desired or used to infiltrate other materials thereby enclosing them into a sealed matrix. Thereafter, setting and hardening is automatic and irreversible. Where concrete is used to form structural elements, it is also natural to use cement in other applications as it minimises potential for materials incompatibility. Thus cement- mainly Portland cement- has been widely used as an encapsulant for storage, transport and as a radiation shield for active wastes. Also, to form and stabilise structures such as vaults and silos. Relative to other potential matrices, cement also has a chemical immobilisation potential, reacting with and binding with many radionuclides. The chemical potential of cements is essentially sacrificial, thus limiting their performance lifetime. However performance may also be required in the civil engineering sense, where strength is important, so many factors, including a geochemical description of service conditions, may require to be assessed in order to predict performance lifetime. The nature of Portland cement is explained. Portland cement is the most widely used cement type and benefits from technology transfer from civil engineering research; also of the more than 150 years of experience of its durability and performance in a range of service environments. The origin of the chemical binding potential of cement arises from a combination of mechanisms: chemisorption on cement solids, incorporation by solid solution in cement solids and, at higher concentrations, precipitation of a solubility-limiting phase or phases in a calcium rich, high pH environment. These favourable potentials, especially pH conditioning, are, as noted, essentially sacrificial: cement must dissolve or react to maintain these conditions in the course of its service life. However the immobilisation potential will also change with time, even in isolation, because cement minerals undergo internal aging and slow reaction with other materials in the near field. Much research has been conducted, often on an empirical basis, leading to the characterisation of these potentials and of their time dependence. Yet the picture which emerges is incomplete and of variable quality. New research is described which, it is expected, will lead to a more scientific basis for the extrapolation of present- day cement performance into the future. The high pH of Portland cement matrices has advantages but also, disadvantages. For example, Portland cement gives excellent protection against corrosion to embedded steel but, on the other hand, it corrodes electropositive metals with evolution of hydrogen. Formation of a high pH "plume" may also spread from the concrete to the near field, degrading other barriers such as bentonite and affecting the sorptive potential of the near field for radionuclides. These considerations have led to the search for alternative lower pH cements which are less alkaline than Portland cement. A description of some common types is given. However alternative choices present a burden of proof because with few exceptions, much less is known about their ability chemically to immobilise waste species and their long- term durability relative to Portland cement in a range of natural environments. It is concluded that the most robust of these alternative formulations are based on calcium aluminate and sulfoaluminate cements, on magnesium phosphate and on geopolymers.

1. INTRODUCTION

Radioactive wastes can be classified in many ways but we observe that the potential hazard poised by a waste, as defined by type and amount of radioactive species in the inventory, is generally accorded priority. Nevertheless, within that classification, it is necessary to have other groupings to facilitate solidification and stabilisation processes. For example, certain wastes such as ion exchange resins and electropositive metals may not be suitable, or are less suitable, for immobilisation using Portland cement but, on the other hand, Portland cement is tolerant of water and hence readily accommodates wet wastes. Thus a waste materials inventory, as well as a hazard inventory, is needed to devise an

effective immobilisation strategy. Moreover, the *inactive* constituents of waste also affect the choice of matrix and processing. For example, organic waste, *e.g.*, cellulosic wastes including paper, may degrade with time, perhaps forming gases such as methane or carbon dioxide, and polysaccharides, which in turn, may complex and solubilise actinides, etc. So a complete material inventory, including inactive as well as active species, as well as a waste degradation pathway, are essential to develop a scenario for the future evolution of physical characteristics such as pH and Eh and of cement-waste interactions. It may be necessary to include and prioritise other relevant degradation processes such as the impacts of microbiological activity.

The repository site may have other geochemical characteristics which affect the disposal scenario. For example, the ground water chemistry of potential sites ranges widely: some sites afford low- mineral pore and fissure water while other sites may have high salinity. Nor is high salinity exclusively encountered in sedimentary rocks: it may also be encountered in igneous and metamorphic terrains especially at depth. For those programmes with designated repository sites, a clear description of the ground water geochemistry is normally available and can be used to guide the immobilisation strategy and repository development. The geochemical description should also include estimates of the impacts of construction and of possible fluctuations occurring in the course of what might be a long operational phase, perhaps ~100 years, and a long (>1 000 years) expectation of barrier lifetime.

Of course many national programmes may be using several repository sites, differing in geochemistry, or have yet to choose a site or sites, or have several sites under consideration. Where a site is still to be selected, the most useful background information about cement barrier performance is generic and indeed, the occurrence of unexpected conditions such as those conditioned by future climate states always benefit from generic approaches to performance. Generic approaches may therefore need to distinguish between two types of site: shallow and deep. Shallow sites are subject to climatic fluctuations, especially seasonal fluctuations. They may be affected by short- term factors such as thermal cycling, wet- dry cycling with episodic flooding. Deeper repositories are arguably less affected by seasonal or longer- term climatic fluctuations but, on the other hand, they may experience thermal cycling from features and processes associated with construction, waste inventory and cement emplacement, for example a thermal pulse arising from the heat of hydration of masses of fresh cement, or from an inventory including heat- generating wastes. Thus the cumulative impacts of a number of events and processes, some of which couple, have to be evaluated.

For all these reasons, the present approach is kept as generic as possible. Once geochemical repository conditions, waste inventory and construction methods are decided, fresh iterations will almost certainly be needed but these will encompass a narrower range of site-specific conditions. The generic approach does, unfortunately, require a great deal of data to reflect potentially broad parametic conditions. At present, we do not have all the necessary data required so, for that reason, subsequent iterations may also require a fresh round of more focussed data accumulation.

This review will largely exclude from consideration those probabilistic factors which influence post - closure performance. For example, repositories may be subject to human intrusion, either deliberately or by accident, or to catastrophic events such as a magmatic intrusion or a meteor strike. Such events will not be treated here.

For alkaline cementitious systems, we note that man- made Portland cements have been in use for only ~150 years. However chemically similar lime - based cements have a longer history of use, perhaps 6 000 years. The Egyptians also made use of gypsum (calcium sulfate) - based cements beginning ~ 6 000 years B.P. So we can access historic structures although, with few exceptions, access with sampling has been confined to those portions which are exposed to the atmosphere. These will almost certainly have had a different history than buried materials, so the performance of historic materials, while of interest, is not always relevant especially to underground environments. Also, the composition of the cementitious materials available today differs from those of historic materials and we have no certain benchmarks with which to establish the properties of historic materials when they were fresh. Nor is the exposure history necessarily well-controlled. For example, the Roman harbour works at Ostia (near the former mouth of the river Tiber) used mass concrete based on lime- activated

volcanic ash, the latter often somewhat altered by hydrothermal processes prior to its use in construction. When Ostia was built the works were clearly intended to provide accommodation for sea- going vessels, *i.e.*, the concrete was exposed to salt water. But at present, these concrete facilities are inland and no longer exposed to salt water. Nevertheless, with care in sampling and inferring the exposure history, examination of historic concretes gives comfort that engineering properties may persist over long time spans, certainly equal to ten half lives of short- lived radioisotopes, *ca* 30-50 years, which imply service lives of 300-500 years or more are attainable.

We also have available in nature so- called natural analogues of cement. These occur where impure limestone, sometimes close in composition to modern cement- making raw materials, have been strongly heated, resulting in the development of many of the same minerals as occur in Portland cement. Heating has occurred perhaps by magmatic intrusion or by combustion of underlying carbonaceous rocks. Subsequent cooling has allowed liquid water to percolate and hydrate the cement-like minerals. Locally, as at the site at Maquarin, Jordan, water percolating these deposits still emerges as high pH springs [1] and a drift built to investigate the engineering stability of the thermally-affected horizon has fortuitously penetrated the cement- rock zone. So, while much of the evolutionary history of the deposits has to be inferred, we do at least know that the pH conditioning ability of alkaline cements containing $Ca(OH)_2$ can be persistent for millennia.

Thus the evidence about cement performance is broadly four – fold, comprised of:

- Results of focussed laboratory experiments on processes affecting cement formation and performance, suggesting potential for 1 000 year (or more) lifetime
- Modelling studies, of expected performance under a range of user- defined conditions.
- Experience of the civil engineering of concrete structures, as recorded in codes of practice and specifications and case studies, and observations on their subsequent durability
- Study of natural analogues and performance of cement and concrete in historic structures and underground characterisation facilities.

Clearly many important questions remain about future performance remain to be answered. But the above evidence provides qualitative assurance that the desirable properties of cement systems can persist over long time periods- at least several millennia and possibly much longer. However they also show that performance life is strongly coupled to the hydrology and geochemistry of the service environment, as well as the amount and chemical characteristics of the waste, now and in the course of degradation.

To establish the foundations of immobilisation science, I concentrate on the evolution with time and temperature of the state of Portland cement. However the work on Portland cements has considerable relevance to other inorganic cements, as will be noted. But knowledge concerning the long-term behaviour of other cement types is variable, so the comparison between cement types is inevitably incomplete.

2. RESEARCH METHODOLOGY

Historically, cement performance has been monitored in three ways: (i) by making field observations on “real” concrete structures, (ii) by making mortars and concrete under controlled laboratory conditions and exposing them to controlled stress, including isothermal ageing, thermal cycles and/or to attack in controlled aggressive conditions and (iii) by studying the behaviour of constituent phases or selected mixtures of phases under conditions such that degradation occurs under controlled and reproducible conditions.

All of these methods have produced useful and relevant results. The nuclear industry has also monitored closely the performance of cement and concrete in underground test facilities, although controlled exposures are of relatively brief duration, a few decades. It has also used accelerated testing

and modelling to compress the time factor but with variable success. Intensification of the attack mechanism, achieved by changing the concentration of attacking salts, raising temperatures or using aggressive solutions, *e.g*, ammonium nitrate, are not much favoured. This is because in real life, the attack process has both fast and slow steps and accelerating selected steps in an attempt to accelerate overall reaction affects the balance between interacting mechanisms, often in unknown ways. Thus intensification is not necessarily realistic. Modelling has, however made huge strides in dealing with complex conditions involving reactive transport and a range of binding processes, as will be discussed elsewhere. And modelling enables reproducible way of extrapolating performance into the future, something which cannot be done from, say, field observations.

It is also necessary to define *performance*. By performance is meant the change with applied stress of some measurable physical parameter. The most frequently measured parameter is compressive strength but equally, other functions such as pH could be measured. Fig 1 shows schematically the change of a selected parameter value with time: when its numerical value has declined to a predetermined, user- defined value, the cement is said to have reached its performance lifetime. Of course a series of relevant parametric values will usually have to be defined, any one of which could fix service life. This concept is valuable because it forces the user to fix the relevant constituent parameters and define minimum parametric values for each. And it expresses clearly the need to reduce "performance" to a series of parameters, each of which is capable of being measured.

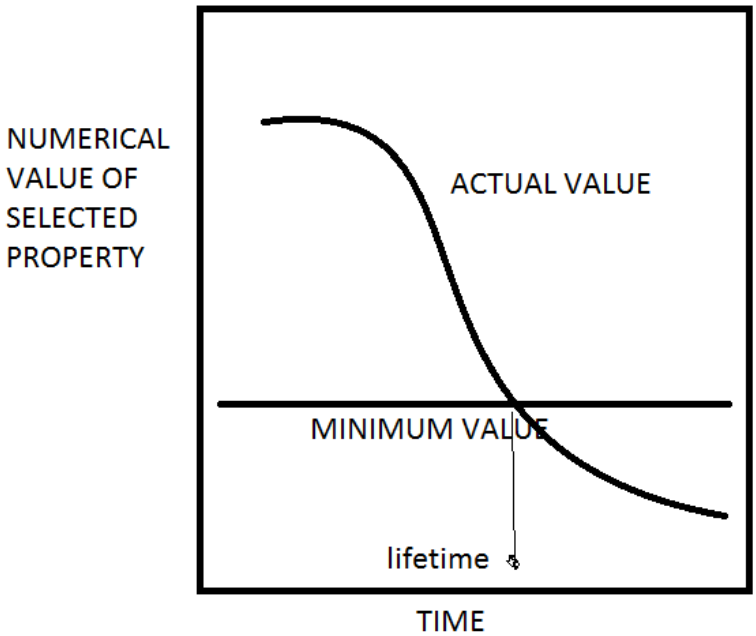

FIG.1. Illustration of the performance concept. The time dependence of selected attributes of performance are determined (actual value) and a minimum acceptable value (horizontal line) of that attribute is defined. A construction line extended from their intersection to the time axis then defines the performance lifetime.

The value of studying concretes in the field is shown by the following example. About 1940, Stanton discovered that certain apparently well- made concretes underwent delayed physical expansion with cracking [2]. Forensic examination of the damaged concrete revealed that the problem arose from the mineral aggregate used; in the presence of water, siliceous aggregates reacted with cement and, as a consequence (as we know today: see [3] for a more modern review) the aggregate underwent hydrolysis. Si-O-Si bonds in the aggregate were broken with formation of siloxane groups (Si-OH bonds). These siloxane bonds facilitated subsequent imbibition of liquid water and the resulting increase in specific volume of the altered aggregate gave rise to an expansive force. When this force could no longer be contained by the rigid but relatively low tensile strength cement matrix, it cracked.

The process is self- accelerating because newly- developed cracks facilitate more rapid ingress of liquid water, as well as other reactive species, resulting in secondary degradation mechanisms. Today we know that this so called "alkali- aggregate reaction", or AAR, is a world- wide problem. But the original observation led to discovery of the process and, subsequently, elucidation of its mechanism. Moreover AAR is often not apparent in short-term tests or examination of structures: typically, decades may be required before signs of distress are evident. But the lesson for design of long- lived nuclear structures is clear: aggregate selection is important, perhaps vital, to ensure performance.

Subsequent to the initial discovery of AAR, many experiments have been done under controlled conditions: the relevant factors, including cement alkali content, were prioritised and systematically varied giving rise to a grid of experimental conditions made using aggregate always from a single source but repeating the experimental grid for each different aggregate. Measured parameters tended to include change in length, and decrease in compressive strength. Yet, while correlations emerged, the correlation coefficients were not always compelling. In an attempt to resolve the problem, expansion was sometimes correlated with measurements of almost any conceivably relevant parameter. This is a classic engineering approach, much used in determining the cause of expansion and response of a material to stress.

Qualitatively, we learned from these empirical studies that sand- sized particles, *ca* 1-5mm, are more damaging to the matrix integrity than either finer, micron size particles or larger particles; a "pessimum" size effect exists, as described in [4]. Also, that the higher the internal pH, the greater is the susceptibility to expansive attack of a particular aggregate, so it is important to limit the Na and K content of the cement as well as the amount of cement per unit volume. Mineralogically, aggregates most susceptible to AAR are found to contain poorly crystallised silica, as occurs in chert, opal, and in many effusive rock types such as rhyolites. We have also learned that susceptible silica varieties can often be distinguished by their undulose extinction when examined under cross- polarised light, using a petrographc microscope. Together, these empirical correlations have been successful in avoiding AAR in new construction. But we cannot necessarily predict future behaviour with a high degree of confidence. The onset of AAR in many structures is simply delayed for 20, 30, 50 (or more) years.

To predict the future behaviour of Portland cement- aggregate combinations, many tests have been developed and some are enshrined in standards. An accelerated test is clearly desirable and the ASTM "autoclave test"(ASTM C 1260) is often applied: standard mortar bars containing the suspect sand are immersed in 1 M NaOH at 80ºC and the physical expansion of mortar bars is measured after 1,3,7,10 and 14 days. Reaction is accelerated both by increasing pH as well as by using elevated temperature. The expansion limit is set at a maximum of 0.1% at 14 days. However the test is known to fail aggregates which, from field experience, give sound concretes and on that account, less severe conditions are often allowed, as for example in ASTM C1293 or CSA A23.2-14A. These tests involve curing mortar bars at 38ºC at ~100% RH; expansion should not exceed 0.1% at 6 months. But this test has also been subject to criticism; the aggregate grading and amount may not correspond to the pessimum (worst case) proportioning and, in any event, expansion is often delayed beyond 6 months. So we do not have a satisfactory way of distinguishing aggregates suitable for design of long- lived nuclear structures. This example highlights the difficulty of devising empirical tests with which to predict the future performance of cement composites. Indeed, it is worth recalling that the fundamental mechanism, of hydrolysis followed by imbibition of water, was only elucidated as a result of careful laboratory experimentation and examination of the underlying physical chemistry [5]. But elucidation of mechanism has yet to be translated into a reliable and dependable test.

Probably the recommended test conditions for AAR - particularly accelerated tests- do not accelerate equally all the relevant factors, so we are still insufficiently informed to know how to model AAR and to translate test results into rigorous selection procedures. In particular, links between "chemical" factors such as temperature, cement alkali content, water/ solid ratio, etc. and "physical" factors such as % expansion, are poorly developed. This interaction between equilibration reactions and kinetics marks many other performance- limiting processes in cement systems with the result that experience of the practical consequences of cement- aggregate interactions remains a valuable teacher. Thus the

example illustrates the importance of experience but also of the dangers of over-reliance on purely empirical correlations to design durable concretes.

We learn that the aggregate, particularly if a siliceous aggregate is selected, represents a major potential source of loss of high pH in the course of reaction with cement. The mass fraction of aggregate typically exceeds that of cement by a wide margin as many engineering concrete formulations contain only 12-15% of cement. Where the nuclear industry has responded to the problem of assessing long- term interactions between cement and aggregate, a common response has been to specify non- siliceous aggregates thereby avoiding AAR. Limestone with a high minimum content of calcite (calcium carbonate) is specified as the aggregate of choice thus avoiding potential Aar problems.

A recent trend has been to model cement performance. But models also have sharp limitations. For example, the chemical/ mineralogical aspects of performance are arguably better characterised than are links between, on the one hand, chemical/ mineralogical change and on the other, engineering properties. As a consequence, modelling has made significant strides in assessing the future states of cement and concrete, for example of its altered state after dissolution and leaching. Modelling requires that we have an adequate database but in addition, I note that:

- In the long term, the phase development of cements will reach an equilibrium property state. Thus, given adequate data and in the absence of mass exchanges, we can predict this state. The equilibrium state benchmarks subsequent calculations, for example of porosity.
- The chemical conditioning ability of the matrix, such as its internal pH and buffering capacity, can be calculated for the equilibrium state and, with adjustment, for non- equilibrium states achieved during early- age performance when hydration of some components, *eg*, slag, fly ash, is still incomplete.
- Metastable phases- of which C-S-H is the most important- can be admitted to calculations provided data are available with which to model. The resulting calculation may be only quasi-equilibrium but nevertheless marks a well-defined and apparently reproducible path. So calculations using mixtures of stable and metastable phases are, with care, valid. However assurance is required, perhaps from experiment or field occurrences, that the metastable state(s) being modelled are realistic and relevant.
- The physical properties of the matrix, such as porosity and permeability, relate partly to process variables and partly to artefacts (*eg* .the initial water: cement ratio, amount of artefact air bubbles and the degree of reactivity of added components such as slag and fly ash). These artefacts cannot generally be modelled. But the physical properties also depend in part on mineralogy, which can be successfully modelled at the current stage of knowledge (a few exceptions and knowledge gaps will be noted subsequently). Progress is being made in evaluating some of the input variables, as for example development of porosity- permeability relationships and their relationship to transport [6].
- The thermodynamic approach to mineralogical evolution suggests that alteration and change of properties in service conditions is best approached by recognising two types of change: *intrinsic* and *extrinsic*. Intrinsic changes occur as a result of isochemical processes: the mass fractions of chemical components remain constant but are redistributed amongst component minerals as a consequence of ageing, or of temperature change, or some combination of changing state variables. Extrinsic change involves mass transport into and/or out of the cement matrix.
- We may also want to relax the strict definition of "isochemical" to include features and internal processes arising from ongoing reaction of some of the supposedly reactive supplementary materials such as fly ash or slag. This amounts to a time-dependent redefinition of the bulk chemistry of the reactive fraction.
- Extrinsic reactions arise because mass transport occurs between cement and its service environment: chemical species are transported into and out of the cement matrix. Mass gains and losses are usually coupled, as for example the need to conserve charge. The species may be those which are abundant in Portland cement, *e.g.*, calcium, or exotic species not normally

present in large amounts in Portland cement, *e.g.,* chloride or magnesium, or both. Coupled transport- reaction codes have to be used for non- isochemical changes and are inevitably much more complex to manage. Significant weaknesses exist in the presently available databases, in particular uncertainties in regard to transport mechanisms and associated numerical evaluation of diffusion parameters and the extent to which they evolve and couple. But as a recent review shows, progress is being made in evaluating and integrating the complex set of equations governing these processes [7].

— Modelling is particularly useful to define boundaries between regimes and in determining the amount of mass transport required to move between regimes. For example, an important distinction arises between regimes in which free calcium hydroxide persists and those which are, and are not, buffered by portlandite. Models thus help guide sensitivity studies and to delineate ranges of conditions where rapid changes occur in characterisation parameters. This, in turn, permits focussed experiments to be devised with which to verify modelling predictions. So models should not be regarded as introducing only greater complexity: they may assist in defining buffered regimes in which properties remain nearly constant across a range of compositions.

The foregoing summary provides a coherent framework in which to progress both experimental studies and modelling. It follows that extrinsic processes are the more complex to evaluate as they may require (i) mass transport over considerable distances and in a chemically- graded system, (ii) consideration of the impact of diffusion through solids which are often porous and (iii) need to treat pore networks which are diphasic*, i.e.*, the pores are only partly filled with liquid. The somewhat uneven progress made in evaluating the performance of cements now and in the future has been highlighted: no single experimental or modelling approach can be used in isolation: what is important is the applicability of the selected methods to the problem in hand, the quality of the data available for application of computational methods, as well as the degree to which independent verifications can be devised. But by employing equilibrium concepts and evaluating key kinetic factors, time-dependent processes and features can in principle be simulated. Natural analogues and experience of historic structures, together with focussed experiments, continue to provide additional reality checks.

3. BINDING OF RADIONUCLIDES INTO CEMENT

The concentration of radionuclide species is important, perhaps crucial, to the binding mechanism and partition between aqueous and solid phases. The exact nature of the binding mechanism has often proved difficult to determine and for that reason, the term “sorption” has often been used collectively to describe all binding process. But in an era of improved quantification, this non- specific usage should be avoided. “Sorption” refers to a surface phenomena whereby radonuclides are retained by weak electrostatic interactions between the aquated species and cement solids. Table 1, after [8], shows a simple classification of mechanisms together with a range of approximate limits over which that mechanism dominates. The upper limit does not imply that the mechanism ceases to operate at higher concentrations, just that it makes only a decreasing contribution to the total binding as other mechanisms dominate.

TABLE 1. BINDING MECHANISMS OF RADIONUCLIDES IN CEMENT

Dominant Bonding Mechanism	**Approximate concentration range**
Sorption	Less than ~10 exp-5 molar
Solid solution	Above ~10 exp-4 molar
Solubility-limiting phase formation	Exceeding 10 exp-9 molar

Several important points need to be made about the relevant processes and features:

— “Concentration” includes the species total in cement, not just concentration in waste. Thus for example a waste might be only micromolar in respect of radio-strontium, but if the cement itself

contains 0.1% SrO (millimolar), the effective total strontium concentration will be orders of magnitude greater than the waste. Higher concentration increases the potential importance of lattice substitution (solid solution) and formation of solubility- limiting phases. Only species not present in nature, for example actinides, Pm and Tc, are exempt from these intrinsic influences.

- Speciation is important in determining binding mechanisms as it affects charge, *e.g*. whether as cation or anion, as well as size and polarisability. Thus low- charged cationic species such a Cs and Sr tend to appear as aquated cations whereas species with high formal positive oxidation states tend to appear as anionic oxy-speciations, *e.g*, Tc(VII) as TcO_4^-
- The cement phases, notably C-S-H with its high surface area and intrinsic nanoporosity, often have numerous sorption sites and it is difficult to distinguish between "surface" and "bulk" sorption processes. C-S-H is known to sorb both cations (Na, K, Cs) and anions (chloride, sulfate, hydroxide) so radwaste species will typically have to compete for sorption sites with other ions abundant in cement [9]. The upper concentration for sorption will thus vary between species and, with rising aqueous concentration, the availability of other binding mechanisms.
- Solid solution is also a possibility, the crystalline solids present in cements acting as hosts. For example, the Al in the AFm phase may be substituted by a range of other trivalent ions e.g., (Cr(III), while the (OH,SO_4) anions normally present in AFm may be substituted by Cr(VI) as CrO_4^{-2}, etc. The host phases collectively offer a large range of sites suitable for substitution of both cations and anions and, given the present state of knowledge, it is not possible to quantify the limits of substitution and site preferences other than by experiment. Finally, at sufficiently high concentrations, the radwaste species may form a solubility- limiting phase. Tin is an example which, at Sn(IV) concentrations > micromolar tends to react with calcium from cement and precipitate as $CaSn(OH)_6$.
- The boundary for precipitation has been fixed rather arbitrarily in Table 1 at ~10 exp-9 molar because all phases have definite solubility in water, the numerical value of which generally exceeds this limit. But for soluble ions, *e.g*., Cs, solubility limits are unlikely ever to be reached except in the course of rigorous drying..

Sorption is often expressed by a distribution ratio, Kd or Rd, depending on whether measurements are reversible or monotropic, *i.e*., approached from only one direction. The concept is simple and robust and has been widely used because each species can be characterised by a single numerical value. But when examined in detail, matters are often more complex. Firstly, data obtained from monotropic experiments should always be regarded as provisional. It is common to undertake sorption experiments across a range of concentrations and the shape of the sorption/ concentration diagram should be inspected for indications that concentration- dependent changes in mechanisms influence the data. Experimental data from complex mixtures of phases, such as cement pastes, are difficult to interpret because of the polyphase nature of the paste: it is not homogeneous and the constituent phases may contribute very unequally to the observed sorption and, moreover, the contribution may be composition- dependant. Experimental problems also arise because some species, *e.g*., Th, Zr, are usually solubilised in strong acid which, when added to cement paste components, destabilises them and contributes significant concentrations of anions not normally present in cement, *e.g*., if nitric acid is used to dissolve the species, nitrate is now present. The solutions may thus develop high concentrations of exotic ions, *e.g* nitrate, with unknown impacts on the phase stability of cement minerals. For example, in the case of nitrate, a nitrate-containing AFm phase is stabilised [10].:its sorption properties for radionuclides are not known.

In some instances, speciation sensitive to redox potential controls the binding mechanism, as for example, iodine, which may be present as iodide (I^-) in reducing conditions but as iodate, IO_3^-, in oxidising conditions [11]. The redox conditions in cement systems will be discussed subsequently but care needs to be taken because ions such as nitrite and nitrate are potential oxidants.

In assessing sorption data note that (i) it is often not possible to verify that the same mechanism operates across the range of composition studied (ii) data may not be determined reversibly and may

contain unsuspected artefacts and (iii) conditions used for the experiments are often not representative of realistic cement environments. The result is that we have much data but its applicability to realistic scenarios is often uncertain. Improved data could no doubt be determined if data were obtained, at least in the first instance, on single cement substances.

4. MINERALOGICAL CONSTITUTION OF PORTLAND CEMENT PASTE AND THE PH FUNCTION

Hardened Portland cement paste consists mainly (95%) of four families of solids coexisting with an aqueous phase. The four solid types are, in approximate order of decreasing abundance, (C-S-H), portlandite, AFm and AFt. The shorthand terms used to designate the solids are defined in Table 2. C-S-H is relatively amorphous to X-ray giving rise to its description as a "gel". In fact the strong irreversible floculation of C-S-H is responsible for much of the strength of hardened cement. Some of the phases shown in Table 2, *e.g,*. AFm, are familial names and significant differences, chemical and structural, exist amongst the individual family members. These differences are probably also reflected in their binding power for specific radwaste species but as yet we have little systematic data.

TABLE 2. SOLID HYDRATES IN PORTLAND CEMENT PASTE*

Shorthand	Approximate formula	Notes
C-S-H	$3CaO•2SiO_2•8H_2O$.	"gel": Ca/Si variable
CH	$Ca(OH)_2$	= portlandite
AFm	$4CaO•Al_2O_3•13\text{-}19H_2O$	Water content variable in stepwise manner in this range. Extensive substitution of sulfate, carbonate, etc. for part of the OH content
AFt	$3CaO•Al_2O_3•3SO_3•30\text{-}32H_2O$	Water content variable in the range $30\text{-}32H_2O$: = ettringite

*The "F" in AFt and AFm is meant to allow for some substitution of Al by Fe. The formulae are shown in "double salt" notation and are not meant to imply structure; much of the "H_2O" is actually present as structural OH (hydroxyl) groups.

The sulfate necessary for AFt formation is usually added to cement clinker as a calcium sulfate (gypsum, anhydrite) in the course of clinker grinding. Modern Portland cement pastes may also contain up to ~5% limestone, itself mainly calcium carbonate. The water/cement ratio required for complete hydration of cement, and hence the amount of pore water, depends in part on the completeness of hydrate development but in general, more water is added to the mix than is strictly necessary for complete hydration; the excess eventually giving rise to "pore water" in hardened pastes. This excess of water is needed for fluidity in the fresh mix. In the hardened product, it is trapped in small, micron- size pores where it dominates the internal chemistry and allows us to apply pH concepts to a solid. The pore water is very real as it can be expressed at high pressures and collected for analysis.

Portland cements typically contain at least 0.4% alkali (Na and K, as oxide %) in the finished clinker. During hydration much of this alkali is readily soluble and, as hydration proceeds, partitions between solid and aqueous phases In the latter, an anion is needed to charge balance the positive charge on soluble (Na,K). However many anions abundant in cement, hydroxide excepted, are rather insoluble, with the result that the alkali is effectively present in mix water and pore fluid mainly as its hydroxide. While the presence of portlandite is sufficient to raise the pH to ~12.5 at 18ºC, soluble Na and K are often present in sufficient quantity to raise the pH of commercial cements to 13 or more. These balances are well- known through pore water expression [12] and their impacts are shown in Fig 2. The band at the top expresses qualitatively the uncertainties. The initial uncertainties result from mainly from different alkali contents, alkali availability for dissolution and different w/c ratios. But the consequences of the alkali content are to raise the initial pH to greater than would be predicted assuming portlandite to be controlling pH.

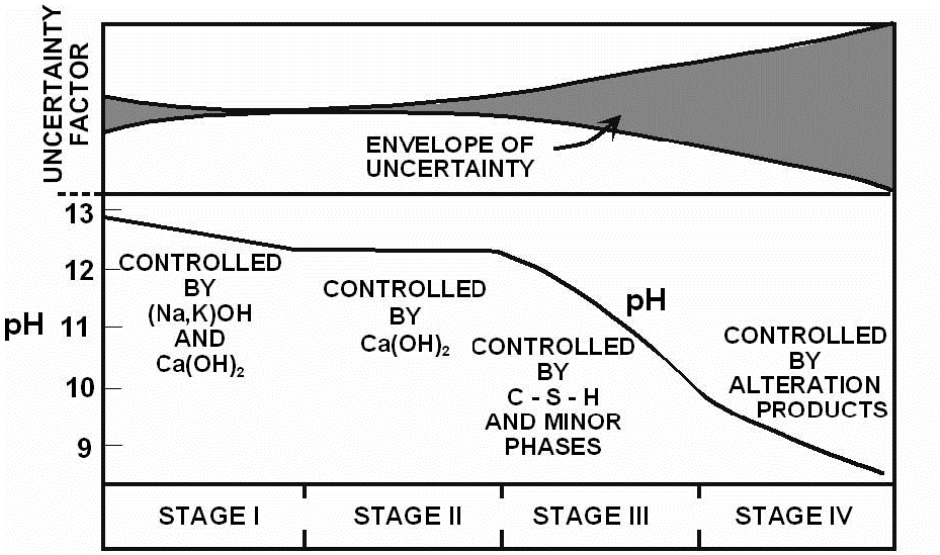

FIG.2. Behaviour of cement in the repository: leaching effects.

However the total amount of alkali in commercial cements is often small, <0.5%, and therefore the buffering capacity of cements to sustain pH above the portlandite threshold may not be high. In other words, pH >12.5 can only be maintained by sacrificial dissolution of the alkali content. However during this phase, of dissolution of alkali, the solubility of calcium is kept very low as a consequence of the common ion (hydroxide) effect.

The most robust high pH buffer is therefore portlandite itself because it comprises much -16-25% - of the mass of cement paste. Thus, while the portlandite pH threshold may be exceeded for a considerable time, for example in fresh cement contained in a sealed drum, once drum perforation occurs and leaching commences, the pH can be expected to drop rapidly to the portlandite threshold. Because pH values above 12.5 are also reduced by dilution of pore fluid in the course of either leaching or mixing with ground water, many scenario treat the high pH stage as ephemeral. Thus, while the super-alkaline state, pH >12.5, may be important in special circumstances, such as in intact sealed containers, its importance to the generation of "alkali plumes" in the near-field environment is perhaps over estimated: pH values above ~12.5 are not well buffered and the capacity to condition percolating water to pH >12.5 is therefore limited by dilution of the relatively small volume of pore water. For example, a ten-fold dilution of an un-buffered pore water, say at pH 13.5, would be sufficient to decrease its pH by 1 unit.

The robust reserve of portlandite, $Ca(OH)_2$ gives rise to a buffered system whose pH performance is predictable and does not depend on the amount of portlandite, and hence has low uncertainty. Eventually, portlandite may be leached although if supplementary cementing materials are added in sufficient quantities, or if reactive siliceous aggregates are present, portlandite may also be consumed by internal reaction. We examine those possibilities, as well as later stages of dissolution and reaction subsequently. But it may be noted that the natural history of evolution of cements divides naturally into four stages, boundaries of which are at the bottom of Fig.2.

The nuclear industry has had difficulty in coping with thermal excursions arising in the course of hydration of matrices rich in Portland cement. The hydration reactions are strongly exothermic and much of this heat is released within the first few days of reaction. Figure 3 shows the heat release as determined in an isothermal calorimeter. The calorimeter performance limits accurate measurements to a few days but this encompasses the main release and gives reliable data with which to translate heat release to temperature rise.

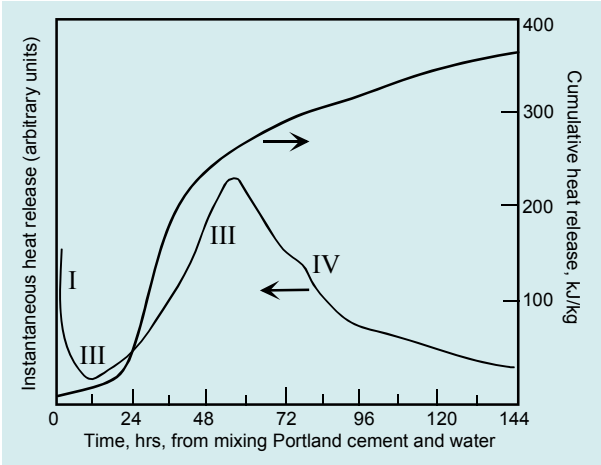

FIG. 3. heat release form Portland cement showing (left hand scale) the instantaneous heat release and (right hand scale, the cumulative release. The cumulative heat release at 144 hours is approximately 2/3 of the total release, assuming 100% hydration.

A frequent response to reducing this initial heat evolution but without markedly extending set times has been to dilute the cement with slow- reacting substances such as coal combustion fly ash and /or ground glassy iron blast furnace slag. These substances are known to react with cement, eventually contributing to matrix formation and, when used correctly, giving low permeability matrices. At the same time, slag and fly ash hydrate more slowly and extend the duration of the hydration exotherm over longer periods of time, such that peak temperatures are reduced relative to a cement-only formulation. In fact, care has to be taken in managing the heat of hydration of slag cements; the heat of hydration of slag is about equal to that of a modern Portland cement but slag hydration kinetics are very sensitive to temperature [13] with the result that, once slag- cement blends reach temperatures above 40-50ºC, slag may hydrate as fast as cement. Thus the goal of lowering peak temperatures in the course of set may only be achieved by careful management of the thermal regime. Because of the difficulty of dissipating heat, this task becomes progressively more difficult as the physical size of monoliths increases. Hence conflict arises between different goals: on the one hand, of reducing the surface area available for leaching, which suggests using large monoliths, but on the other hand, avoiding thermal cracking. the severity of which correlates well with increasing monolith size Engineers have often sought to reduce the peak exotherm by using supplementary materials but, as noted, the resulting thermal regime depends on, amongst other factors, scale, and is not generic.

Fly ash is a complex material containing both crystalline and amorphous phases but most work has been done in the nuclear context with low- lime, high (Al+Si) ashes - the so-called class F ashes. The glassy fraction of these ashes comprises the majority phase, perhaps 75-90% of the total ash [14]. But the high concentration of "acidic" components in the glassy phase ensures that fly ash is reactive with portlandite contributed by cement. Generalised data on the % portlandite consumed by fly ash is hard to obtain partly because of the inhomogeneous and variable chemical nature of fly ash, partly because of the slow reaction kinetics and partly because of the greater complexity of the hydration products. However, neither slag nor low- lime fly ash will themselves generate portlandite in contact with water. At best, therefore, they dilute the portlandite arising from Portland cement and at worst, they react with consumption of portlandite. Low- lime fly ash in particular hydrates with strong consumption of portlandite. Indeed, a well known test for fly ash reactivity involves measuring the diminution of portlandite content with time in mechanical mixtures of initially known proportions of fly ash and portlandite [14].

The nuclear industry takes comfort from the fact that, measured after a few month, Portland cement-fly ash blends apparently reach a steady state but retain high pH, *ca* 12.5. However microstructural studies disclose that considerable potential for reaction remains; reaction is still on-going, albeit slowly. Gordon [15] reported on the mineralogy of an aged 60% fly ash- 40% cement blend moist cured for 8.4 years at 20º, 55º and 85ºC. The pH of the matrix, after grinding and mixing with a small

amount of water and measurement at 20ºC, had declined to 11.8 (following 20ºC cure) and 11.5 (following 40ºC and higher temperature cures). Free portlandite had been reduced to <1% (the estimated limit of detection) at all temperatures. This experimentally observed mass balance agrees with thermodynamic predictions: fly ash in excess of ~25% contributes sufficient aluminosilicate glass to consume all the portlandite as well as begin partially to decalcify C-S-H.

The literature with regard to portlandite consumption by slag is not consistent and it appears that, depending on slag composition, slag may consume variable amounts of portlandite but that, in general, most commercial slag compositions will be net consumers of portlandite. Thus the long- term maintenance of high pH in blends, particularly those containing large amounts of cement replacement, is far from assured even in the course of isochemical reaction. Modelling the long- term behaviour of these compositions is handicapped by lack of data on the mineralogical nature of the phases formed and of their thermodynamic properties. But an important conclusion for nuclear engineers is that the chemical and mineralogical variability of slag, and especially fly ash, is much greater than that of Portland cement so that it is unrealistic to treat these materials as having a single reaction pathway with cement or that late stage reaction is simply a prolongation of the early stages.

Considering first the behaviour of plain Portland cement, about which we have more certainty, once portlandite has been consumed (as, for example, by leaching or reaction), C-S-H, AFm and AFt phases still remain to condition pH. But in slag blends the constitution of the AFm phase evolves stepwise with time and, in response to the increased activities of alumina and silica the AFm evolves towards strätlingite, an AFm-structured phase close to $2CaO.Al_2O_3.SiO_2.8H_2O$ in composition.

The role of C-S-H in controlling pH becomes more important as stage II gives way to stage III (as defined in Fig.2) because it comprises the main pH- stabilising solid. Certainly, as portlandite is depleted the C-S-H need not be lime- saturated: its Ca/Si ratio is free to decrease giving rise to pH less than ~12.5. This corresponds to the boundary between stages II and III, Fig 2, and shows that leaching is not the only mechanism whereby pH can be decreased. Three types of change may affect the pH conditioning ability of C-S-H, as shown in Table 3. Arguably the best studied of these factors is the effect of changing Ca/Si ratio on pH.

TABLE 3. FACTORS AFFECTING THE PH CONDITIONING ABILITY OF C-S-H

Factor	State of knowledge
Ca/Si ratio	Reasonably well understood: pH decreases smoothly with decreasing Ca/Si
Substitution of minor components into C-S-H (Al, SO_4, etc)	Systematic study lacking, but no evidence that substitution changes pH by >0.5 unit
Annealing/ Thermal cycling	Extent of change and its impacts not well characterised and changes are difficult to benchmark: see text
Crystallisation	Data mainly for >100ºC; only incomplete data at <100ºC

The impact of Ca/Si ratio on pH conditioning ability shown in Figure 2, after Pabalan, *et al* [16], relates mainly to calcium solubility because each soluble calcium generates approximately 2 negatively charged (OH) ions per Ca.This can be transformed to pH from the definition of pH and the relationship that: $Kw = [H^+] [OH^-] = 10 \text{ exp-}14$ at 25ºC, where Kw is the ion product of water.

The single curve depicted averages many recorded data sets, each with significant standard deviation, so the accuracy with which pH is known is not as high as the figure might suggest. The solubility data for Si (not shown) also scatter rather more than for Ca: the low Si solubilities, typically micromolar at high Ca/Si ratios, are, however, difficult subjects for accurate analysis. The limits of C-S-H gel formation extend between Ca/Si molar ratios ~0.8 and ~1.7. Within this range, single- phase gels can be prepared; the measurements in Figure 3 are based on gels made in the laboratory and hence not

affected by chemical impurities. After averaging and smoothing, the results appear to give a continuous smooth curve with saturation pH values ranging from ~10 to ~12.5 at 20ºC.

Ca -rich C-S-H dissolves incongruently in the sense that the ratio of Ca/Si in the aqueous ratio is different- and in this case, greater than- that of the solid. However, as the solid Ca/Si ratio decreases, calcium solubility also decreases and silica solubility increases with the result that solubility approaches congruency; this point is reached at Ca/Si~1.0. So the solubility mechanism, as well as the absolute solubility, of C-S-H changes with Ca/Si ratio.

The chemical analysis of C-S-H in Portland cement is, however, subject to significant uncertainties. Portland cement paste is polyphase and, even at the high magnification and despite the good spatial resolution of modern electron analytical methods, it is difficult to distinguish between incorporation of chemical species, *e.g.* Ca as $Ca(OH)_2$ or Ca and Al as AFm as distinct from solid solution. It would, however, appear that the substituent Al in the C-S-H of Portland cement is only present up to a maximum Al/Si ratio ~0.05 at ~20ºC and that Ca/Si ratios >1.5 in single phase C-S-H are only attained by intercalation of a calcium- rich phase. At this point, and once a steady- state distribution is reached, most- if not all- of the Al in C-S-H is in tetrahedral coordination substituting for Si. The compensatory charge balancing mechanism is uncertain: it could be accomplished by adjustments to the OH content, or by alkali substitution or by a combination of mechanisms.

A unique feature of C-S-H is that it sorbs both cations and anions from high pH solutions; in commercial cement, Na^+ and SO_4^{2-} are probably the most important sorbed species and on that account, have been much studied [17,18]. There is however no indication that these substitutions significantly (+/- 0.5 unit) affect the pH conditioning ability of substituted C-S-H although, on account of the many uncertainties about the structural state of these ions, it is difficult to obtain properly benchmarked values. Evidence is that sorption and desorption are essentially reversible within hours or days, at least for sulfate.

Many amorphous metastable phases can maintain constant composition but undergo *annealing* while still preserving their essentially non- crystalline character. Annealing involves a change in internal state but not a change sufficient to develop the long- range atomic or ionic ordering characteristic of crystalline substances. Optical glass is an example: annealing the glass at temperatures well below its softening point allows local atomic relaxations to occur and the resulting small atomic movements are sufficient to affect its physical properties, such as density and refractive index, while still preserving its glassy non-crystalline nature. For C-S-H, solubility changes in the course of annealing are arguably more relevant indicators of changing internal states. Of course it has long been suspected that the internal state of C-S-H depends on preparation history. X-ray diffraction patterns of laboratory C-S-H are less diffuse, *i.e.*, more crystalline, than the C-S-H of commercial cement but the origin of the differences in powder pattern is not clear. Taylor [19] summarises the historical distinction between C-S-H types, distinguishing a type I and II on the basis of crystallinity. Indeed, significant solubility differences have been claimed depending on the mode of preparation of C-S-H [20-22]. However, the range of reported ph values is not large: for a fixed composition, they do not vary by more than ~0.2-0.4 pH unit. But the interpretation of literature data in terms of varying solubility have not been accepted generally and more work is needed to corroborate and explain the supposed differences. The practical implications of the existence of significant annealing effects would be that, in the absence of portlandite, a general decline in pH conditioning ability could occur spontaneously as a consequence of ageing. At present, the existence of annealing effects in homogeneous C-S-H sufficient to affect pH are possible but not proven. Indeed, proof will almost invariably rely on operative criteria to define the internal state of C-S-H as distinct from other causes of changing solubility (solid solution, presence of other components and phases, etc.)

Arguably, the main hazard to the persistence of gel-like C-S-H is crystallisation. Crystallisation might also be expected to have the biggest impact on properties. Indeed, studies in the literature have frequently used elevated temperature to induce crystallisation of C-S-H. In this respect, autoclaving cements, using steam cure to accelerate crystallisation is a well-established industrial practice. It is known that the C-S-H of commercial cement crystallises readily, within hours, at temperatures above

~150ºC. Strength is lost and porosity increases in the course of C-S-H crystallisation. However the products of crystallisation depend on bulk Ca/Si ratio as well as temperature: Table 4 shows the stable assemblages at low temperatures according to the current state of knowledge. The data, taken from [21], have been modified to take account of the now known Ca/Si ratio of jennite at 1.5.

TABLE 4. STABLE $CaO-SiO_2-H_2O$ SOLIDS (Ca/Si <0.8) AT <120ºC

Range of Ca/Si ratios	Temperature,ºC	Phases present
>1.5	>100	Portlandite, afwillite
>1.5	<100	Portlandite, jennite
1.0-1.5	>100	Afwillite, xonotlite
1.0-1.5	<100	Xonotlite, jennite
0.83-1.0	<120	Tobermorite, xonotlite

Industrial experience of autoclaving mainly lies in the range above 120-150ºC, higher temperatures, *ca* 150-180ºC, being used to ensure faster reaction. It is known that the low strength of autoclaved cements is due to the relatively high density of the crystalline products which, when formed from low density precursors such as gel -like C-S-H, give rise to enhanced internal porosity. It is not however inevitable that strength decreases upon crystallisation: adding reactive silica sufficient to lower the Ca/Si ratio from its normal range in Portland cement, 2.5 to 2.9, to ~1.0 to 1.5 results in rapid (18-24 hr) reaction at 160-180ºC and nearly complete crystallisation of the C-S-H, while still retaining cohesion and strength. This is because the mineralogical nature of the crystalline products depends on temperature, duration of treatment and effective Ca/Si ratio of the sand-cement mix. By adjusting the Ca/Si ratio in the range 0.8 to 1.5, yields of either (or both) tobermorite or xonotlite are maximised. Their formation results in little change in the specific volume of the solids, with consequent preservation of strength. Note also that quartz- normally regarded as unreactive- is virtually consumed in the course of reaction,

The crystalline calcium silicate hydrates have lower solubility, and hence lower equilibrium pH, than the corresponding C-S-H gel; data are shown in Table 5.

TABLE 5. SOLUBILITY AND PH CONDITIONING ABILITY OF RELEVANT CALCIUM SILICATE HYDRATES

Crystalline Phase	Ca/Si	pH	pH of equivalent gel
Gyrolite	0.66	8.3	-
Tobermorite (11Å)	~0.83	10.3	11
Xonotlite	1.0	8.4	11.5
Afwillite	1.5	10.3	12.4

The pH of crystalline phase assemblages will vary in stepwise fashion whereas that controlled by gel is continuously variable, at least over the Ca/Si range of homogeneous gels. Unfortunately we do not at present have solubility and pH data for jennite.

The practical implications of crystallisation can be envisaged as follows. Figure 4 shows the state or condition of the cement in several time frames. The stated conditions are derived from known data but the size of the envelope of conditions (time, temperature, pressure) necessary to move from one state to another are not well established.

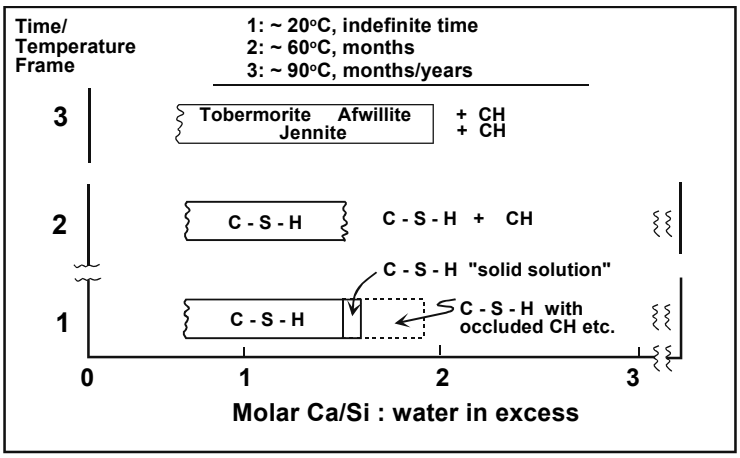

FIG. 4. Possible phase assemblages in Portland cement. The state of fresh cement is depicted in state 1; state 2 depicts the situation where the maximum Ca/Si ratio of C-S-H gel decreases to 1.5, resulting in increased portlandite production. State 3, the equilibrium state, results from crystallisation of C-S-H gel.

The composition of a fresh Portland cement projects on Fig 4 at Ca/Si in the range 2.5-3.0. Thus all three states retain portlandite and, as a result, have a high pH. However if the bulk Ca/Si ratio is decreased, as may occur by reaction, *e.g.*, by reaction with sufficient fly ash, by carbonation, or by leaching, or by some combination of mechanisms, the mean Ca/Si ratio decreases and the evolutionary path is no longer dominated by portlandite; complex paths are possible. Scenario 3, crystallisation, is especially effective in decreasing the pH in the portlandite- free range of Ca/Si ratios.

Thus at high Ca/Si ratios, the pH is dominated by portlandite and the pH does not change significantly with crystallisation. However, at Ca/Si ratio <1.5, the consequences of crystallisation depend on Ca/Si ratio. If gel persists, the pH declines steadily and regularly with decreasing Ca/Si ratio but if crystallisation occurs, the solids may instead consist of afwillite, xonotlite, tobermorite or appropriate mixtures and the resulting aqueous solubility follows a stepwise trend. Thus an abrupt drop in pH occurs at and below Ca/Si = 1.5. The solubility of xonotlite itself is low and this gives rise to a singular point on the solubility curve.

As we have shown, the effective Ca/Si ratio of cement can be lowered in three ways; (i) by adding sufficient reactive siliceous materials, possibly including mineral aggregate but more likely deriving silica from sources such as fly ash, which reacts with calcium thereby lowering the effective Ca/Si ratio of C-S-H or (ii), by leaching, which at high Ca/Si ratios, dissolves Ca much more extensively than silica; in the initial stages of dissolution, the ratio of aqueous Ca/Si is ~1000 and (iii), by crystallisation, resulting in formation of a series of crystalline compounds. The consequences of reduced pH conditioning have to be evaluated in the context of the repository scenario: the pH may reduce but on the other hand, assuming a constant flux of leachant, the lowered solubility of crystalline phase assemblages implies longer lifetime relative to the “gel” model.

On the other hand, the evolution of sorption potential with crystallisation is not so readily predicted. As described, the gel has a general sorption for both cations and anions and it is well known that the zeta potential of solid C-S-H varies with composition in a systematic way, becoming more negative as the Ca/Si ratio decreases. Thus calcium- rich C-S-H tends to be a better sorber of anions than of cations but this order will gradually reverse as the Ca/Si ratio of C-S-H decreases below ~1.1 at which point the sign of the zeta potential changes. On the other hand, experience of crystalline substances shows that their sorption potential is not dictated primarily by composition but rather by highly structure specific factors. Crystalline structures may provide sites which are (i) accessible to ions in solution and (ii) electrostatically suitable and of the right physical size to sequester the species. Classical surface science and the concept of an electrical double layer have of course been applied to sorption- desorption but (i) the distinction between “surface” and “bulk” is not easily made for nanoporous materials such as C-S-H and the applicability of classical theory isuncertain.

The influence of structure, as distinct from composition, is shown by considering the sorptive properties of zeolites. Zeolites are arguably the best- known example o selective inorganic sorbers: their crystalline architectures contain cavities ranging in size according to which structure is described but in general, have cavities capable of accommodating atoms, ions and molecules. The cavities are sometimes closed but are sometimes accessible through channels or openings. Once filled, species bonding and retention occurs by weak secondary electrostatic interactions. Neutral species can also be bound by dipole- induced dipole forces. Because the cavities are internal, surface area does not limit sorption and, as a rule, bonding sites are available in large numbers because of the three- dimensional nature of the host structure. However a glass or gel of the same composition as, say, clinoptilolite zeolite, would be expected to lack these stereo-regular cavities and to differ by orders of magnitude in sorption properties, with zeolite showing much the higher sorption and with great preference for particular species, *e.g.*, Cs or Sr. It should be noted that while zeolites are not generally encountered in cements, many natural analogues of cement do contain zeolites coexisting with typical cement phases: also that fly ash- rich blends approach the range of bulk chemistries in which zeolite formation might be expected in the longer term.

Although the structures of most of the relevant crystalline cement phases are known, such as ettringite (AFt) we are as yet unable to predict their sorptive properties in detail but it appears that "sorption" potential is mainly dominated by ion exchange. However organic molecules are often well held at surfaces.

How likely is C-S-H crystallisation to occur in actual applications? At present we can only answer this question qualitatively: the probability of crystallisation will increase with the duration and severity of thermal excursions. C-S-H gel is certainly thermodynamically metastable with respect to crystalline solids under all conditions. But neither the crystallisation kinetics nor mechanism(s) are at present well understood. However, comparing difference between the structures and ordering in the gel precursor and its likely crystallisation products(s), a nucleation and growth mechanism seems most likely to control the course of crystallisation. Gels lack the long- range order characteristic of the equilibrium products. But, on the other hand, a supposed structural similarity exists between local structures in the gel and at least two of the crystalline phases known to stable at low temperature, jennite and tobermorite, with the result that a continuous transformation from a structured but essentially disordered gel to a crystalline substance cannot be excluded.

On the other hand, the composition of C-S-H in plain Portland cement paste, Ca/Si ratio ~1.7-2.0, differs from the Ca/Si ratio of jennite (1.5) and crystallisation of the gel would also require nucleation and crystallisation of portlandite: that is, the reaction would be inhomogeneous. What is needed to resolve speculation about crystallisation mechanisms is (i) a better mechanistic understanding of how crystallisation occurs at temperatures below ~120ºC; is it continuous or discontinuous, and does mechanism depend on composition? (ii), creation of a time- temperature -transformation diagram, to establish the crystallisation kinetics and persistence of C-S-H gel over time for key compositions. These studies would link to a determination of pre-crystallisation annealing effects in C-S-H. These additional data would, in turn, enable a more realistic assessment of the impacts of heat- generating inventory and of heat evolution of the evolution of chemical and permeation properties of grout. It will also provide a better starting point for calculating the leaching and pH evolution of cement barriers in the post closure phase, when temperatures have returned to ambient.

It is well -established that thermal treatment also affects the physical properties of cement paste and that the impact depends on *when* the thermal pulse occurs. Most cements subject to heat treatment in the course of early (0-30 day hydration develop a "two-tone" texture when examined by back-scattered electron (BSE) imaging [23]. Optically, C-S-H found enveloping cement clinker grains looks to be more reflective than hydration product formed in interstitial spaces. The latter probably formed by solution- precipitation processes whereas the former probably developed by direct attack of water on clinker particles. These two C-S-H types are termed "inner" and "outer" hydrate respectively; the two types of C-S-H are often seen together with apparently sharp interfaces even at magnifications typical of scanning microscopy (X100-10000). Normally, the optical brightness of a phase increases with both its mean atomic number and density. But much work on microchemical analysis of "inner"

and “outer” C-S-H product has failed to disclose significant *chemical* differences between them so it is supposed that the observed differences in BSE reflectivity may arise from differences in porosity and water content [24].

Much effort has been devoted to study of the microstructure of cement pastes in order to link properties with structure, especially at the nano- and microscale. These efforts have given useful insights into processes occurring in the course of hydration and ageing. For example, porosity can be visualised directly. For example, it is well known that the permeability of slag- cement pastes is lower than that of Portland cement although the measure % porosity is often, within limits of error, the same. Fig 5 helps explains why this should be so.

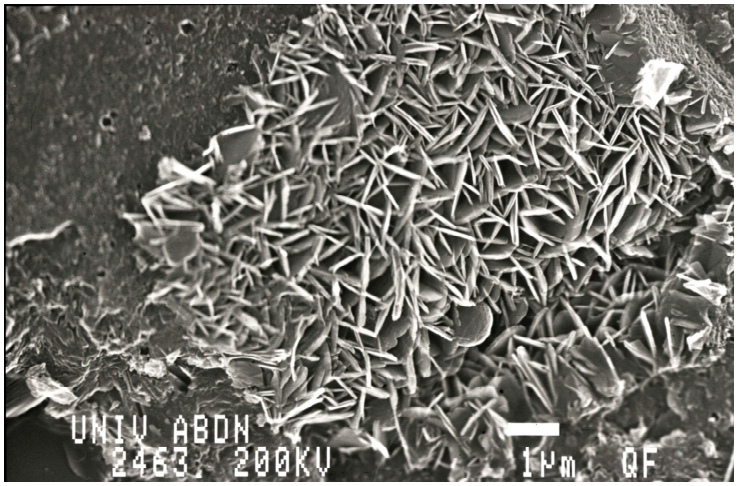

FIG.5. Micrograph of a former slag grain in a Portland cement blend after several years hydration at 25°C. The white bar near the lower right hand corner is 1 micron.

The slag grain, originally homogeneous glass, has reacted with Portland cement forming mainly platelets of a hydrotalcite- like phase (magnesium aluminate hydrate) The platelets show in sharp relief because internal porosity has also developed as other species originally present in the slag, for example Ca and Si, have diffused into and densified the matrix. This process does not much change total porosity but by concentrating and isolating pores onto the site of former slag grain, reduces the permeability.

Despite difficulties in explaining the origin and quantifying the complex microstructures of heat-treated cements, it is generally agreed that the porosity of cement paste increases with severity of heat treatment. For example, Verbeck [25-27], using fresh cement cured at selected temperatures, recorded considerable increases in porosity with rising cure temperature: a selection of results is shown in Table 6. Absolute porosities of cement paste are difficult to measure and some techniques only sample a defined size range. Nevertheless, different measurement techniques identify broadly the trends described above and are indicative of the large differences, particularly amongst pores in the coarser size range, resulting from elevated cure temperature. Since transport properties are most affected by the volume of larger pores, it follows that elevated temperature cure will degrade the permeability and hence impair the physical barrier function. This is especially so as the BSE evidence indicates that the increased porosity arising from warm cure is not distributed uniformly but instead concentrates in the interstitial C-S-H phase. This concentration tends to increase the degree of interconnectivity of the coarse pore network and hence has a disproportionate effect on facilitating transport. It is frequently noted that very low permeations reported for laboratory samples, typically made on small scale and not subject to thermal excursions, fail to be achieved at full scale. Thus the extent to which the thermal excursion in large masses affects porosity are not necessarily correctly evaluated in the course of small-scale trials, which tend to give overly optimistic estimates of permeation properties.

TABLE 6. POROSITY OF PORTLAND CEMENT PASTE AS A FUNCTION OF CURE TEMPERATURE

Method	Size range	Cure temperature/porosity,%		
		5ºC	20ºC	50ºC
Mercury Intrusion	<700Å*	0.21	0.22	0.23
Backscattered Electron Microscopy	2 500-12 500Å	4.27	10.93	15.11

* The value obtained from intrusion strictly defines a pore entry diameter.

In the above experiment, hydration occurred mainly at the temperature shown. Other studies have shown that -perhaps unexpectedly- clinker hydration is retarded at high temperatures, >50ºC approximately [28]. Reasons for this retardation are not clear, but it appears possible that (i) free water necessary to continue hydration, once removed from the vicinity of hydrating grains, is not readily replaced and (ii) the "inner hydrate" forms a dense, relatively protective coating around clinker grains thus protecting or partly protecting them against subsequent hydration. This effect, of retardation of clinker hydration in elevated temperature regimes, is characteristic of cement formed in large monoliths. Physically large masses are subject to a self-generated thermal pulse from the heat of hydration. But in some cases, as in a repository containing heat- generating waste, the thermal excursion may be much delayed, until after much or all of the cement has hydrated. Paul and Glasser [29] showed that cure at normal temperatures, followed by prolonged cure, *ca* 8 years, at elevated temperature resulted in conversion of much of the paste minerals to hydrogarnet. The hydrogarnet formed at elevated temperatures had a composition intermediate between that of grossularite garnet, $Ca_3Al_2Si_3O_{12}$, and hydrogrossularite, $Ca_3Al_2(OH)_{12}$. The silica necessary to form hydrogarnet must of course come from C-S-H; relative to ambient benchmark cure, C-S-H decreased in amount and also reduced in Ca/Si ratio to ~1.5 or less. These mineralogical changes did not affect pH because portlandite was not consumed in the course of the above reactions and, indeed, it may have increased in amount. But the higher density of garnet relative to its solid precursors, coupled with its formation in a solid whose external dimensions remain essentially constant, gives rise to much increased internal porosity.

The experience with pastes in which 40% fly ash replaced Portland cement show that portlandite is consumed rapidly, within a decade, at elevated temperatures, 40ºC and above [15]. Mass balances for these cements are achieved by combining the portlandite with (Al,Si) oxides. These are mainly furnished from fly ash glass, giving strätlingite, $2CaO.\ Al_2O_3\ SiO_2.8H_2O$; strätlingite is a member of the AFm family containing an aluminosilicate interlayer anion. It largely replaces other AFm phases in matured cement pastes with high levels of slag replacement. Notably, some of the mineral constituents of fly ash nominally regarded as un-reactive, *e.g.*, mullite, $3Al_2O_3.2SiO_2$, are also partially consumed after 8 years at 85ºC [15]. Ettringite was also not found and presumed to be unstable at the elevated temperature; the sulfate thus released was believed to have been incorporated into hydrogarnet where it substitutes for silicate.

5. PRACTICAL IMPLICATIONS FOR DETERMINING THE FUTURE STATES OF PORTLAND CEMENT

One important implication emerging from these studied is that important scale effects occur in the course of setting and hydration of Portland cement. A modern Portland cement has a heat of hydration in the range 450-500 J/g of which roughly half may be liberated within the first 3 days of hydration at ~20°C. In tests at laboratory scale, the rapid initial heat evolution is readily dissipated and the cement does not experience significant temperature rise. But larger masses approach adiabatic behaviour; it becomes increasingly more difficult to dissipate heat without resort to cooling and, as a result, considerable self- heating of the setting mass may occur. The effect is well known in civil engineering experience where the thermal excursion has to be carefully managed, in part by limiting the size of consecutive casts as well as the time interval between casts. The temperature rise is itself a complex function of cement and water contents, the cement type, presence of heat sinks, if any, such as mineral

aggregates, of monolith geometry and total mass, as well as the thermal conductivity of the concrete surroundings and materials of construction of moulds. However, commercial computer-based routines are available with which to predict and manage the thermal excursion.

Like all materials, cement and concrete has a thermal coefficient, expanding with heat and contracting when cool. The magnitude of its coefficient depends in part on the mineralogical nature of the aggregate used is similar to that of steel and common rock types, *ca*. 7-10 ppm/ºC. But, during the initial stages of heat evolution, the cement is normally still sufficiently fluid so that no stress accumulation occurs in the course of self-heating. As an approximation, strength gain sufficient to permit stress accumulation begins at or near the thermal heat evolution maximum, with the result that the main stress results from contraction, consequential on self-cooling in the course of cooling to ambient temperature. Since cement is intrinsically brittle and has low tensile strength, .its normal response to excess stress is to crack. Thus large masses of even well- made concrete material may crack spontaneously although, where the thermal stresses are well managed, the cracks will be closely spaced and small, *i.e.,* microcracks. Microcracks are, however, rarely straight- through and, as a result of size and limited length, will not much affect the permeation properties. However a situation to be avoided is the development of few but large cracks; this will lead to disproportionate degradation of the permeation properties. Thus, in good practice models used by civil engineers, the thermal pulse is managed using both thermal models and, if necessary, actual full scale trials. The nuclear industry needs to make fuller use of this experience and not rely on the results of small-scale trials as proof that cracking will not occur. Scale effects are important and have a definite bearing on concrete quality. On the other hand, chemical properties can be measured on products of small scale trials and the results scaled up often without serious error.

The foregoing discussion concentrates on thermally- induced cracking. Of course there are other causes of shrinkage and cracking. Notably, the conversion of a solid powder plus water to a solid matrix consisting of cement paste hydrates (possibly with a slight excess of trapped water) involves a change in dimension. Normally, a little shrinkage, *ca* 0.01-0.05% in linear dimension, occurs and this is considered to be desirable to (i) facilitate demoulding of cast products and removing formwork and (ii) preventing stress accumulation when, for example, concrete is cast with restraint. The shrinkage occurring during isothermal hardening is termed *chemical shrinkage* but other causes of shrinkage, for example drying shrinkage, are well known [30].

Manufacturers will often adjust the cement composition, particularly the content of interground calcium sulfate, so as to control shrinkage. Typically, adding more sulfate reduces chemical shrinkage. However shrinkage compensation is partly an art, partly a science and, where high replacement levels of supplementary cement materials occur, as for example, when adding much fly ash or slag, the balance between too much and too little shrinkage compensation may require extensive trials. Shrinkage in nuclear construction assumes great importance because a common method of controlling thermal and other dimensional changes used by civil engineers, of including “expansion” joints, may not be an attractive option for monolithic barrier constructions, in forming seals, etc.

Much emphasis has been placed on the pH of cement matrices. As has been discussed, the high pH is both a source of immobilisation potential but also may affect the stability of other barrier materials: the impact of pH can be beneficial, as for example in affording corrosion protection to embedded steel, or harmful, as in its potential for hydroxide and calcium attack on bentonite with loss of its swelling properties. But the numerical value of pH is not the only relevant factor in evaluating the persistence with time of the chemical immobilisation potential. Before we can establish future performance, we need to evaluate the buffering power of the cement, that is, its ability to maintain pH against degradation. The natural environment is only rarely at high pH so a great range of degradation processes will operate spontaneously as the system attempts to reach an equilibrium. For a selected few species, the pH effect is absent or of little significance: Cs and Sr are examples of species whose solubility limits are high and essentially independent of pH. But for most species, the first step in assessing binding reactions with cement and the loss of *chemical* potential for immobilisation is to fix a point at which cement ceases to perform (see Fig. 1). Thus, for example, the solubility of many actinide species is greatly reduced at pH >10 so we may wish to define the loss of immobilisation

potential at the point where pH declines to ~10. In fact, this is a convenient point to choose for benchmarking performance as all the abundant solids in Portland cement paste are capable of conditioning pH to >10, so complete destruction of the phases normally present in the cement matrix has to occur before cement ceases to function with respect to this pH. However if we wish to fix the limit somewhat higher at, say, pH 11.5, the calculation becomes more complicated: we need to know how the cement degrades and for this, we may also need site specific geochemical and hydrological data.

We can, however, be confident of the data for $Ca(OH)_2$; it dissolves congruently and being crystalline, has constant and fixed properties which are independent of the amount of substance. Thus one way of defining the buffering capacity would be to use the point at which the content of $Ca(OH)_2$ fell to zero to mark the end of performance. Indeed, many models use this point for benchmarking, for example in the original Berner model [31], where simple dissolution is assumed to be the main factor controlling decline in performance. For example, if a kg of Portland contains 25% portlandite*, i.e.*, it contains 250 g of portlandite per kg. of cement, and if the portlandite solubility is 1.1g/l, the cement would require to equilibrate with~ 227 kg of initially pure water to dissolve all the portlandite. If the dissolving solution were not water but, say, sodium chloride, the solubility of portlandite would be enhanced especially in the range of NaCl concentrations ~0.5M (approximately sea water concentration) by a solubility factor increase in the range 2 to 3, depending on temperature [32]. Thus calculations based on exhaustion of $Ca(OH)_2$ alone, while not very accurate, are relatively simple and usefully serve to benchmark results from more sophisticated calculations.

Measuring performance against the portlandite threshold is almost certainly overly conservative: for example, cement continues to protect steel against corrosion (in the absence of chloride) to as low as pH ~10.5: radionuclide solubility, particularly of actinides, remains low at pH <12 and insolubilisation extends to pH possibly as low as 10. Indeed, many fly ash blended cements are depleted in portlandite but continue to give satisfactory service. As noted, fixing the pH for exhaustion of chemical immobilisation potential at a lower value than the portlandite threshold, in the vicinity of~10.5 has another advantage: it coincides with the minimum pH conditioned by low- lime C-S-H.

Thus we have a natural choice of two states to define performance limits: the portlandite exhaustion point and the C-S-H exhaustion point. If we assume dissolution occurs into a constant flux of pure water, and that a simplified cement consists of 25% portlandite and 75% C-S-H, we see by reference to Fig. 2 that the Ca solubility decreases from ~22 mmomlar for portlandite to ~1.5 mmolar for calcium-poor C-S-H. Correspondingly, the dissolving power of water for calcium will decrease by a factor of~ 15 as the solid composition evolves between these points; this reduced solubility will give a marked increase in performance lifetime defined in terms of the number of water exchanges required to deplete the pH conditioning value.

In real life, other factors may affect the evolution of the solid phase composition and the duration of high pH conditioning. In laboratory simulations, variables can be assessed singly but in disposal environments, several factors may couple. For example, carbon dioxide, either in gas or dissolved in ground water, reacts with both portlandite and C-S-H forming calcium carbonate. Once dissolved carbon dioxide enters the calculation- and few natural waters do not contain sufficient dissolved carbonate strongly to interact with cement- calculation of its impacts will almost certainly require application of a computer code: the balance between dissolution and precipitation depends on too many factors for simple graphical analysis. But in general, carbonation will shorten the performance lifetime.

If crystallisation occurs, such that C-S-H gel is reconstituted into the equilibrium calcium silicate hydrate assemblages, the basis for analysis of the performance lifetime again changes. At the high Ca/Si ratios typical of commercial Portland cement, ~2.5-3.0, rather more portlandite forms in the course of C-S-H crystallisation than if gel were present. Indeed, portlandite persists stably to Ca/Si ratios as low as 1.5. This gives rise to a “step” in the pH *vs* composition curve: at Ca/Si ratios <1.5 the pH declines abruptly but still remains slightly above pH~ 10 for compositions extending to as low as the tobermorite ratio, Ca/Si ~0.83: at this point, the pH conditioning of gel is less that one pH unit

higher than that of the equivalent crystalline phase. A special point arises at xonotlite, Ca/ Si = 1.0, which is very stable and has an exceptionally low ability to condition pH. It thus creates a "xonotlite trap". If a cement paste were to decalcify homogeneously to Ca/Si~1.0 and crystallise, converting entirely to xonotlite, its equilibrium pH would diminish to below the threshold (~10) for acceptable pH conditioning. However, while it is unlikely: that large masses of cement would participate homogeneously in any process that lowers pH *e.g*, leaching or carbonation,: the weak pH conditioning power of xonotlite is unique and cannot be neglected.

As noted, more data are needed especially on the kinetics of crystallisation processes. Based on present evidence, crystallisation- perhaps induced by heat from radioactive decay- will affect the pH evolution but is unlikely significantly to reduce the total amount of buffering reserve per unit mass on account of the stability and persistence of portlandite amongst the crystallisation products. However, cements have a number of physical functions to perform in the repository and property changes other than pH conditioning also need to be considered.

6. IMPACT OF THERMAL EXCURSIONS ON THE PHYSICAL PROPERTIES OF PORTLAND CEMENT BARRIERS

The impact of warm cure during the initial hydration of cement has been described and the increase in porosity with rising temperature has been noted. This increase in porosity results from three causes (i) the changing composition of the gel-like C-S-H phase C-S-H formed at higher temperatures has progressively less water which, in turn, reduces the ability of the solid to fill space, (ii) the decreasing stability of AFt with rising temperature, resulting in formation of physically denser phases (relative to the Aft precursor) and (iii) crystallisation, with the stability of hydrogarnet increasing with rising temperature. Relevant densities for the calculation of space filling are given in [33]. Factors (ii) and (iii) are related: AFt, on account of its low physical density, has good space filling ability while that of hydrogarnet, with its high physical density relative to its precursors, creates additional pore volume and increases the permeation while also decreasing strength. In general, once cement has hardened, its external geometric dimensions are not much affected by subsequent mineralogical changes, especially those leading to formation of denser solids: instead, the diminished molar volume of the constituent solids increases the internal porosity in the course of transformation. Sufficient of the additional porosity is interconnected to increase the permeability. On the other hand, reactions of type (ii) are reversible: with decreasing temperature, AFt can reform at the conclusion of a thermal excursion: the consequences are discussed below. Thus the mineralogical balances in a cement paste are very sensitive to temperature although the time taken to establish the temperature-dependent equilibrium varies widely. In general, reactions occurring spontaneously with rising temperature occur more rapidly than those on the cooling cycle. While the relationships between reaction rate and kinetics, as well as the links with physical properties such as densification, porosification and permeability cannot at present be fully quantified, the trends are evident. It follows, therefore, that where it is desired to utilise the physical barrier action of cement to the fullest, the barrier itself should preferably not be subject to thermal excursion either in the course of construction or subsequently, in service. The above text gives reasons why thermal excursions are best avoided but another important reason can be given: the reversibility of temperature- dependant reactions with temperature and its physical consequences.

As an example, the long- term instability of heat- cured cements may be considered. For decades the concrete pre-cast industry has been concerned about turnaround time for moulds used to form complex shapes, with the result that curing in warm or hot water has been used to speed hardening and facilitate recovery and recycling of moulds. Shortly (typically within a few hours) after production with a heat cure cycle, the hardened product will meet strength requirements. However in the course of prolonged storage and/or in service, heat cured products are frequently found to lose strength and physically expand. These effects may not become apparent for months or even years. Research has shown that an important source of delayed expansion is associated with excessive cure temperature in the early history of the concrete, in the course of manufacture; AFt, normally present in hydrated paste, becomes less stable at elevated temperature and reduces in amount [34]. The sulfate thus liberated from AFt in the course of warm cure is redistributed amongst pore fluid and other solids, notably AFm and C-S-H. But subsequently, and typically at much lower temperatures than were used for thermally

accelerated cure, the lower temperature equilibrium mineralogy is regained. This process requires an induction period lasting perhaps months or years. However, once equilibrium begins to reassert itself, AFt re-forms and its low physical density leads to a physical expansion which cannot be accommodated within the original volume, with the result that physical expansion occurs. Reasons for this are not entirely clear: expansion occurs even though the matrix may contain empty pores which could, in theory, accommodate the newly-formed ettringite without expansion. Clearly, although the driving force for expansion is the restoration of equilibrium, the sites for preferential crystallisation of ettringite are such as to generate expansion.. The term "delayed ettringite formation", or DEF, is used to describe this phenomenon and associated processes. DEF remains a serious obstacle to warm or hot curing of concrete. It should also be noted that DEF does not generally superimpose on normal thermal shrinkage, which is rapid, because of the sluggish nature of the causative reactions of DEF: the two processess occur at different times At present, given the cement composition and temperature extremes, we can predict a potential for expansion, but not the actual expansion.

DEF is avoided primarily by limiting the thermal excursion: it may also help avoid DEF by using low-alkali and low sulfate Portland cement. But these are areas of contention. Note, however, that while thermal cracking depends primarily on the temperature *difference* between the high and low thermal point in the cycle DEF depends on the solubility relations of Aft, and hence on the *maximum effective temperature attained*, *i.e.* the temperature which best fits the mineralogy actually attained in the course of a warm cure or thermal excursion.. This maximum is linked to cement chemistry and hydration kinetics and, although the links are not well quantified, from experience the practical upper limit of accelerated thermal cure should not be allowed to exceed ~50-55 ºC.

7. REDOX CHARACTERISTICS OF PORTLAND CEMENT

The concept of redox potential is well established in geochemistry, as are its two complimentary characterisation parameters, *poising capacity* and *electroactivity*. By poising capacity is meant the resistance to change of the numerical value of Eh, the redox potential (analogous to buffering in discussion of the pH function). Electroactivity measures kinetics: some redox couples which might potentially affect the redox potential appear to be very inert, while others are active.

The Eh of normal Portland cement reflects its manufacture under relatively oxidising conditions: measured Eh values lie in the range +100 to +200 mV (potentials given here are relative to a standard hydrogen electrode at 25ºC). However the Eh of Portland cement is not well poised and may be affected by redox- active substances. For example, embedded steel corrodes slowly and is redox active, combining with free oxygen and liberating hydrogen, with the result that in the absence of oxygen gain, perhaps from an external source or radiolysis, the internal redox potential may decrease to as low as ~-550 mV.

The electroactive substance may also be part of the cement system. Thus many blends used in waste immobilisation are formulated with 20-90% iron blast furnace slag. Recalling that the purpose of slag in the iron- making process is to remove sulfur from the metal, the slag glass often contain ~0.8-1.0 wt% sulfur. This sulfur is present as sulfide ions believed to substitute for oxygen in the glassy phase structure. These sulphide ions are released as the slag hydrates. The impact of slag on Eh depends partly on age because (i) slag reacts only slowly with water and cement, so sulfide release occurs over long time periods, perhaps decades or centuries, and (ii) the first sulfide to be liberated reacts with free oxygen and is oxidised to sulphate and does not influence the Eh: Eh lowering requires 30-40% slag minimum (depending on composition and reactivity). For example, if the Eh is measured after 28 day ambient temperature cure the measured Eh of slag –rich formulations decreases into the range minus 200-350 mV. It is believed that the buffering couple poising the Eh depends on the equilibrium between sulfur species, mainly between sulfate and thiosulfate, $(S_2O_3)^{-2}$ The importance of the couples with chemically reduced sulphur species is that they are very electroactive. For example, chromium (VI) is not well immobilised in Portland cement, where it persists as hexavalent Cr,but in appropriate slag blends, the sulphide/ thiosufate reduces Cr to the (III) oxidation state: the latter species is very effectively bound into cements [35, 36]. It is likely that many actinides would be reduced to lower- and less soluble- oxidation states in slag cements. However, very little

systematic work has been done on tailoring the redox potential of cement systems so as to enhance their immobilisation potential for redox- sensitive nuclides. This goes hand in hand with developing agreed protocols for the measurement of poising capacities in cement systems.

Fly ash often contains "reduced" iron, mainly as magnetite (spinel) as well as unburnt carbon. In theory, this carbon should lower the Eh but, in practice, this couple appears to be kinetically inert and does not participate, at least over laboratory timescales of a few years, in affecting the internal redox potentials of fly ash composite cements.

Numerous opportunities for affecting Eh could in principle arise from reactions of cement components with gas, *e.g*, CH_4, H_2, arising from processes such as waste degradation and metal corrosion. as well as from the impact of ionising radiation on cement pore fluids. For example, radiolysis of water produces, amongst other species, peroxide, which can bind well to cement substances. On the other hand, hydrogen generated in the course of radiolysis is not bound and may not be retained. Radiolysis is of course a very complex process and its long- term impact on the redox potential of cement systems not well established. Thus radiation may have potential to alter the redox behaviour of Portland cement although we have little systematic information of the evolution of redox potentials and poising capacities in cement matrices impacted by ionising radiation..

8. NON-PORTLAND CEMENT

Mention has been made of other inorganic cement types. The history and state of knowledge concerning these cements varies greatly from one type to another: for this reason, information on these cements is divided into two types: those with a history of use in construction and those which are long known, but not used in structural applications. Representative examples are listed in Tables 6 and 7 respectively. Those listed in Table 6 are known to give good corrosion protection to embedded steel but it may be noted that some "acidic" formulations cannot be expected to be protective.

TABLE 6. ALKALINE NON- PORTLAND CEMENT TYPES

Type/designation	Standards and codes	pH	Handling characteristics	Remarks
Calcium aluminate, CAC. Commercial product	Yes	~11-12	Supplied as powder and activated by mixing with water, like PC	Protective to steel
Calcium sulfoaluminate, C$A. Commercial product	Yes	~11-12	Supplied as powder and activated by mixing with water, like PC	Protective to steel

The two alkaline cement types shown in Table 6 have a relatively long history of use; for CAC, of more than 100 years but for sulfoaluminate types, only since the 1970s. Both types have high heats of hydration and liberate much of this heat within the first 24 hr of hydration, so the initial hydration exotherm needs careful management. Both types are, like Portland cement, supplied as powders ready for use requiring only mixing with water. They may be used to form grouts, mortars and concretes and are compatible with most mineral aggregates except those containing gypsum or other calcium sulfates. The freshly mixed product has a period of fluidity during which it can be poured, pumped or delivered in the same way as Portland cement. As with Portland cement, much of the added mix water becomes chemically combined in the course of setting and hardening, so the permeation properties of hardened mixes depend on the amount of excess water remaining after the hydration demands of the cement have been satisfied. However the water requirements for complete hydration depend on which type is used: for CAC, low w/c ratios, *ca* 0.4 or less, are required to obtain matrices with low permeation. The sulfoaluminate types are generally formulated so as to generate much AFt as the matrix- forming solid and, since AFt has a high bound water content, rather more water is chemically combined than for CAC. Therefore, it is relatively easy to formulate C$A cements so as to achieve

self-desiccation as hydration progresses, *i.e.*, to achieve a dry internal environment. Mixtures of CAC and Portland cements have also been used where extremely rapid set is required. However these mixed cements generally achieve at best low strength. On the other hand, both C$A and CAC types have been used successfully to repair previously hardened Portland cement, to which they adhere well.

Thus, both C$A and CSA have well- established technologies [37]. For example, fresh cements may require a set retarder to extend workability of fresh mixes. Therefore commercial products will almost invariably be supplied with a proprietary retarder. If the intention is to avoid organics, special cement types are unlikely to meet this restriction unless an inorganic retarding system is specified.

With regard to performance in service, most is known about CAC. It has, as noted, given outstanding service in aggressive environments, being more resistant to both sulfate and acid attack than Portland cement. CAC cement is however, weakened by prolonged service in warm, humid environments. It undergoes a process termed "conversion" whereby calcium aluminate hydrates of the AFm family transform spontaneously to the more stable hydrogarnet. This process, termed "conversion", in the course of which a low density phase is converted to one of higher density represents thermodynamic equilibrium and cannot be prevented. Its consequences lead to a decrease in strength and an increase in porosity which, in turn, degrade the permeation properties of hardened products. Temperatures above 20ºC in moist service should therefore be avoided. It is probable that adding slag to CAC changes the mineralogy and avoids the conversion problem, but insufficient long term experience is available to assert with confidence that the stabilisation is permanent. C$A cements, with their high content of AFt, are prone to dehydrate in warm, dry environments.

Sulfoaluminate cements were developed in China in the 1970s and most of the relevant standards and historical indicators of performance are of Chinese origin The use of C$A cement outside China has been mainly, but not entirely, confined to specialist and non- structural applications: for example, as active components of tile setting cements, in self-levelling floor screeds and in mine stabilisation. No significant generic problems appear to have been encountered in any of these applications, nor have adverse experiences been reported in China. However ettringite, a main binding mineral of the hydrated matrix, becomes unstable at elevated temperatures and at low relative humidity, so it would be prudent to avoid these conditions: service in hot, dry environments is not recommended. In China, much use has been made of sulfoaluminate cement concretes where its rapid hardening properties lend themselves to formation of pre-cast products. Experience of samples removed form various service environments of both normal and pre-cast products has been reported [38]. It is believed that carbonation upon exposure to normal air may be more rapid in sulfoaluminate concretes than in Portland, but in making a comparison with Portland cement, it is difficult to ensure that formulations so different in chemistry are really equivalent.

Some other types of cement are shown in Table 7. These cements are often not commercially available, so with few exceptions they will not be supplied as premixed single powders (although with ingenuity, some could be marketed as single- pack formulations) The cementing action is typically achieved by mixing an acid and a base. For example, magnesium phosphate cements are typically made by mixing a base (solid and fine-grained periclase, magnesium oxide) with an "acid", such as potassium monohydrogen phosphate. Hardening occurs slowly but spontaneously upon mixing the two components and, to ensure a period of workability, it may be necessary to add a set retarder. The products of hydration are a series of "basic salts", magnesium hydroxyphosphate hydrates. Both acid and neutal cements can be obtained, depending on CaO/P_2O_5 ratio. Typically, the hydration products do not include amorphous, gel- like phases but instead gain strength by developing an interlocking network of needle or bladed crystals. However, despite the generally low pH ,phosphate has a strong passivating action against steel corrosion. A report elsewhere in this volume by Langton describes the development and application to nuclear wastes of phosphate cements in the USA: much of the underlying knowledge base relevant to their use in nuclear applications appears to have been established.

The hydroxyhalide cements are also well known. These are made by stirring fine-grained periclase (magnesium oxide) into a concentrated aqueous solution of magnesium chloride. These cements were

once widely used as flooring screeds and decorative finishes, *e.g.* ornamental mouldings. However their use in nuclear waste applications cannot be generally recommended for three reasons; (i) they are too water soluble and loose coherence upon prolonged wetting (ii) in the course of dissolution, they liberate soluble chloride, a potential complexant for radionuclides and (iii) the liberated chloride is very corrosive to steel.

We may therefore concentrate on the phosphates. Like the oxyhalides, phosphate cements typically consist of a two solid component mix, an acid, usually a phosphate salt and a base, typically calcium or magnesium oxide. Until recently, most of our experience with these cements has been at small-scale: typically they have been used in repair of bone or teeth and as specialty refractory and tile fixing mortars. Some of the matrix formers, such as apatite, $Ca_5(PO_4)_3(OH,F)$ have great persistence in nature and have potential for use as matrices for waste encapsulation and on that account are good candidates for durability in the long term.

The problem about understanding phosphate cements is the great range of chemical components and compositions which are potentially cementitious. There is general agreement that processes which liberate ammonia are probably not suitable for radioactive waste immobilisation. If this is accepted, it would rule out compositions based on ammonium phosphates even though some formulations bind ammonia as ammonium ions, for example by forming matrices composed of $Mg(NH_4)_2(H_2PO_4)_2.4H_2O$, $MgNH_4PO4.\ H_2O$ and/or $MgNH_4PO4.6H_2O$ or, where sodium is present, $NaNH_4HPO_4.4H_2O$. However the susceptibility of ammonium salts to biodegradation and stability under irradiation is still to be determined.

As noted, the calcium phosphate cements may be of more interest on account of the permanence and geological persistence of the solids: one possible objective is to form good yields of the most stable and least soluble phosphates, such as hydroxyapatite,$(Ca_5(OH)(PO_4)_3$,and brushite, $CaHPO_4.2H_2O$.

The proportioning of these cements is often dependent on the reactivity of the starting materials. MgO in particular is slowly reactive and rate-limiting so it is often deliberately added in excess. This poor reactivity means that initially, the other components, which are frequently acidic, will dominate the pH. But eventually, when the acidic component is consumed, the excess of MgO may be sufficient to shift the pH into the alkaline range. Thus phosphate compositions are potentially useful, although many practical problems, *e.g.* very short workability times and scale- up effects such as high heat evolution in the course of set, have to be overcome before they can be applied with confidence. We also know less about their long- term property evolution in the repository environment relative to other constructional cements. It is also particularly important to determine the water balances, which are not always intuitively apparent on account of the complex nature of reaction products and sluggish hydration kinetics but, if low permeability is desired, it is important that most of the water added should be chemically combined. On the other hand, many phosphates formed from high valent metals, e.g. tri- and tetravalent lathanons, and actinides, are known to form extremely insoluble phosphates which, moreover, are durable and resistant to degradation in natural environments.

TABLE 7 .REPRESENTATIVE PHOSPHATE CEMENTS

Type/designation	Reactants	Comment
Silicophosphate	$CaSiO_3$ (wollastonite) and H_3PO_4	Initially, strongly acidic
Sodium phosphate	Sodium heaxametaphosphate, water + other hardeners	Fine grained MgO may be added.
Ammonium phosphate	Reaction of MgO and sodium/ potassium phosphate forming a variety of magnesium ammonium phosphate hydrates	Rapid set and strength gain
Calcium phosphate	Mixtures of calcium phosphates in suspension to form brushite or hydroxyapatite	CAC cements can also be used
Zinc phosphate	Mixtures of ZnO and H_3PO_4	Main experience is in dentistry
Potassium magnesium phosphate hydrates	MgO and K_2HPO_4 or KH_2PO_4	Described in this report by Langton

Another and entirely different matrix type is formed by mixing aqueous solutions of sodium hydroxide, potassium hydroxide, or of the respective alkali silicates, with an aluminosilicate solid. This solid could be fly ash, calcined kaolin, or various other clays, itself usually activated by heat in a previous step. Such compositions have been termed “geopolymers”. The name is not well chosen because the raw materials, especially NaOH, KOH and thermally altered clays, are either unknown or rare in nature: thus they do not have a history of natural occurrence and persistence and the prefix “geo” is misleading.

On the other hand, the most successful of these formulations give as reaction product, a non-crystalline and -surprisingly- water insoluble matrix, with a pH much less than would be expected from their high content of alkali hydroxide or silicate. It is apparent that much of the alkali becomes bound into a rigid gel- like solid phase and that the properties of this gel are fundamentally different than those of C-S-H gels occurring in conventional Portland cement. Much work has yet to be done on these materials to define the nature of the bonding agent and its properties, especially the likely durability and persistence of the binder in the range of natural environments envisaged for repositories. It is known that the gel binder tends to crystallise at “warm” temperatures, ~60ºC and above, and that the crystalline reaction products tend to have less strength than the precursor gel. So it is likely that they cannot be recommended where a significant thermal pulse is anticipated.

The problems about using these matrices are, realistically, numerous. We lack (i) long term experience of their performance in a range of service environments (ii) characterisation of their reaction with waste and other materials present in the near field, (iii) extent and mechanism of binding between the matrix phases and radwaste species and (iv) information on scale-up effects: in the absence of data on their heat evolution, long term dimensional stability, reactions with waste and evolution of porosity and permeability in hardened properties. These and many other relevant thermo-physical properties necessary to a well- found safety case are still to be quantified.

However if an alkaline environment is desired, but at a lower pH than Portland cement, magnesia-based backfills comprise a matrix whose mineralogy is relatively simple and consists at least initially of well characterised solids. MgO itself is a weak base, much weaker than CaO. The equilibrium phase in contact with water is brucite, $Mg(OH)_2$. Of course the reactions of brucite with substances in the service environment are more complex: for example, carbonation of brucite leads to formation of a series of magnesium hydroxy- hydrates, *e.g.*, hydromagnesite, $Mg_5(CO_3)_4(OH)_2.4H_2O$, but finally forming magnesite, $MgCO_3$ as the product of complete carbonation. Nevertheless, magnesia- based systems are more susceptible to characterisation than some of the systems listed in Table 7, with the possible exception of apatite- brushite assemblages, and remain possible candidates for alkaline but “low pH” matrices.

9. CONCLUDING DISCUSSION

The presentation has concentrated mainly on Portland cement This concentration is justified by (i) the considerable extent of knowledge about Portland cement and its behaviour in a wide range of service environments, (ii) its compatibility with steel, and the protection given by Portland cement against corrosion, (iii) the availability of Portland cement, made worldwide to very similar standards, (iv) its versatility, including compatibility with other reactive supplementary cementing materials such as slag and fly ash, compatibility with remote and automated formation methods and ease of meeting other engineering and safety constraints and finally, (v) the steady increase worldwide in the inventory of waste which has already been cemented with Portland cement.

An important chemical characteristics of Portland cement is its high alkalinity. Not only is it capable of conditioning water to pH>12 but the cement solids have a large buffering reserve, so the resulting pH is maintained in robust manner: the buffering capacity of cement is large. These chemical properties can be assessed from laboratory scale studies and have been successfully modelled. At the high pH of the matrix many (but not all) radioactive waste species are insolubised.

The physical properties of cement barriers are, however, subject to scale effects. For example, full scale construction often fails to achieve the low permeability which can be demonstrated in the laboratory. Reasons for this are complex but arise mainly because of dimensional changes occurring in the course of solidification processes. Not only does shrinkage occur but dimensional changes- mainly shrinkage- may be exacerbated by the exothermic heat of hydration. Better appreciation of the importance of the early formation stages and the consequences to final properties, leading to management of the early stage thermal pulse associated with hydration, are emphasised.

The high pH of Portland cement brings both advantage and disadvantage. For example, a combination of high pH and low poising capacity provides positive corrosion protection for mild steel; this protection, being robust, is likely to persist until degradation is well advanced. Additionally, Portland cement has a useful chemical immobilisation potential: as noted, it binds many radionuclides by a variety of mechanisms, sorption at low concentration but at higher concentration, in solid solution with the matrix- forming phases as well as formation of solubility- limiting phases. These binding actions are unique and still require more characterisation on a species-by- species basis to clarify the fundamental mechanisms and the range of concentrations over which they operate, as well as the evolution of these potentials in the course of cement ageing and degradation. The binding mechanisms combine significantly to reduce the mobility of many radionuclides and play an important part in the safety case. On the other hand, the high pH of the matrix, combined with its high buffering capacity, may influence the near- field mineralogy. For example, repository design often seeks to benefit from the swelling properties of bentonite clay to form seals and barriers but montmorillonite clay (the main active component of bentonite) is subject to deterioration reactions at high pH. Proximity to cement may be sufficient to sustain reaction and fundamental materials incompatibility may preclude use of both bentonite and cement barriers.

The beneficial pH- conditioning action of Portland cement is essentially sacrificial. As cement dissolves, a high pH plume is generated in regimes of low, semi- static ground water flow with the result that cement sorption properties of minerals in the near field may be affected: the example of bentonite has been discussed. This effect, of conditioning circulating ground water to high pH, is referred to as the “alkaline plume”. It is generated by the cement portion of the barrier and, in some cases, the minerals of the near field may undergo reaction and degradation at the high pH. However, concerns about the role of the “alkaline plume” need to be kept in proportion. It is true that mineral alteration and degradation induced by the plume may make questionable the value to the safety case of batch sorption tests done on minerals in the near field but, on the other hand, it is possible that alteration from the alkaline plume may actually be beneficial for retention, as for example by converting feldspars to zeolites. Moreover many common minerals in fractures, e.g., dolomite, react with and mitigate the alkalinity, of high pH plumes. The substitution of “low pH “cements for Portland cement, expressly to avoid problems which may not in practice exist, creates many new uncertainties about how to assess the performance of these materials over long time scales. Some criteria are

advanced to guide the search for “low pH” cement matrices and it is suggested that types already in use be given priority; unproven formulations require a major research effort.

At the same time, important uncertainties persist about the future of Portland cement barriers. Foremost amongst these is the evolution with time and temperature of the metastable phase, the C-S-H gel binder, which typically comprises >50% by mass of Portland cement. In barrier applications with intended performance lifetimes in the range 300-500 years, evidence from historic cements which have not been subject to thermal excursions, suggests that C-S-H will persist, so the safety case can rest on C-S-H properties obtained on aged materials. At present, we are uncertain about the nature and severity of ageing effects. However in the extreme case, C-S-H will crystallise. The best present evidence is that, should this occur, the crystallisation products will continue to condition pH, albeit in some composition ranges to a lower numerical value than for fresh cement. But overall, the reduction is believed to be of limited significance, less than 1-2 pH units. Moreover, by virtue of the decrease in solubility attending crystallisation, the performance lifetime at pH ~10 should be extended because of the decreased solubility. Crystallisation of C-S-H may, however, impair the mechanical strength and enhance the permeability of cement barriers.

Most Portland cement is combined with mineral aggregate into concretes, grouts and mortars. There is potential in the longer term (>100-1 000 years) for siliceous aggregates to react with cement. This factor, the impact of aggregate on long term performance, has probably received insufficient attention in assessing performance lifetimes especially when cement-based products are used in warm, wet conditions.

All barrier materials and systems represent a series of compromises, between what we know and what we do not know, as well as between presently- identified advantages and disadvantages. It is important to weigh these factors carefully and define the envelope of acceptable performance. If the geochemical parameters of the disposal environment are not known at the outset, the process of optimising barrier performance may have to be done by an iterative process, accepting that a few environments may be inimical to cement performance and that severe material incompatibility problems could arise. Thus the selection of conditioning matrices and design of the engineered barriers ought to be an integral part of the site selection process.

In the past, the nuclear industry has relied on observation on cements in natural exposures, supplemented by testing under laboratory conditions. This approach has yielded qualitative but valuable results. However this approach fails to lead to a predictive capability: no proven methodology exists with which to extrapolate results into the future. Moreover, cement formulations change with time: for example, the development of self- compacting concretes is a recent and welcome development albeit not anticipated in historic constructions. Increasingly, therefore, performance-based analyses will be done by modelling.

The modelling process is faster, cheaper and more flexible than experimental programmes and hence much favoured. It is true that modelling is far more flexible than experimental grids and better able to address the time factor; experiment lacks a systematic basis for extrapolation between data points and inevitably lack extension beyond the grid of conditions and maximum duration selected for study. But the reliability of a computer- based model is also subject to potential errors and its reliability rests on (i) the applicability of the scenario selected for evaluation (ii) the quality of its data available to sustain calculations and (iii) the nature and soundness of any experimental verifications performed in support of model\predictions. It is thus necessary to maintain a robust experimental capability in support of modelling. Indeed, the combination of the two approaches, experimental and modelling, is often much more powerful than either modelling or experiment in isolation.

REFERENCES

[1] "Maqarin Natural Analogue Study" (SMELLIE J.A.T., Ed.), SKB Technical Report TR-98-04 (in 2 volumes), Swedish Nuclear Fuel and Waste Management Company (SKB), Stockholm (1998).

[2] STANTON, D.E., The Expansion of Concrete Through Reaction Between Cement and Aggregate, Proc Amer. Soc. Civil Eng. **66** (1940) 1781-1811.

[3] GLASSER, F.P., "Chemistry of the Alkali-Silica Reaction", The Alkali Silica Reaction In Concrete (SWAMY, R., Ed.), Blackie and Sons, Glasgow (1991) Chapter2, 30-53.

[4] HOBBS, D.W., Alkali Silica Reaction in Concrete, Thomas Telford, London (1988).

[5] DENT-GLASSER, L.S., KATAOKA, N., The Chemistry of the Alkali-Aggregate Reaction, Cement and Concrete Research **11** (1981) 1-9.

[6] GLASSER, F.P., MARCHAND, J., SAMSON, E., Durability of Concrete: Degradation Phenomena Involving Chemical Reactions (Proc of the 12th Int. Congress on the Chemistry of Cement, Montreal , CA), National Research Council of Canada (BEAUDOIN, J., Ed.) (2007).

[7] ELAKNESWARAN, Y., et al., Ion-Cement Hydrate Interactions Govern Multi-ionic Transport Model for Cementitious Materials, Cement and Concrete Research (2010) (in press).

[8] STUMM, W., MORGAN, J.J., Aquatic Chemistry (3rd Ed.) John Wiley, New York (1996).

[9] GLASSER, F.P., HONG, S.-Y., Alkali Sorption by C-S-H and C-A-S-H gels, Part II: Role of Alumina, Cement and Concrete Research **32** (2002) 1101-1111.

[10] BALONIS. M., GLASSER, F.P., Densities of Cement Phases, Cement and Conc.Res. **39** (2009) 733-739.

[11] ATKINS, M., GLASSER, F.P., Encapsulation of Radioiodine in Cementitious Waste Forms, pp 15-22 in Scientific Basis for Nuclear Waste Management, XIII (OVERSBY, V.M., BROWN, P.W., Eds), Materials Res. Soc., Pittsburgh PA **176** (1990).

[12] BARNEYBACK, Jr., R.S., DIAMOND, S., Expression and Analysis of Pore Fluids from Hardened Cement Pastes and Mortars Cement and Concr. Res. **11** (1986) 279-285.

[13] UCHIKAWA, H., Effect of Blending Components on Hydration and Structure Formation (Proc. of the 8th Congress on the Chemistry of Cements, Rio de Janiero), Vol 1 (1986) 249-280.

[14] LONGUET, P., BURGLEN, L., ZEIWER, A., La Phase Liquide du Ciment Hydrate, Rev. des Mater. **1** (1973) 35-41.

[15] GORDON, L.E., Impact of Prolonged Warm (40º and 85ºC) Moist Cure on Fly Ash - Portland Cement Paste, MSc Thesis, University of Aberdeen (undated).

[16] PABALAN, R.T., et al., Review of Literature and Assessment of Factors Relevant to Performance of Grouted Systems for Radioactive Waste Disposal (final report on Contract NRC -NRC -02-07-006), Center for Nuclear Waste Regulatory Analyses, San Antonio, TX (2009).

[17] SKAPA, R., Optimum Sulfate Composition of Portland Cement, PhD Thesis, University of Aberdeen (2010).

[18] HONG, S.-Y., GLASSER, F.P., Alkali Binding in Cement Pastes-The C-S-H Phase Cement and Concrete Research **29** (1999) 1497-1504.

[19] TAYLOR, H.F.W., Cement Chemistry (2nd ed.), Thomas Telford, London (1997)

[20] JENNINGS, H.M., Equilibria Between Aqueous Phases and Two Types of Calcium Silicate Hydrate, Jour. Amer. Ceram. Soc. **69** (1986) 614.

[21] HONG, S.-Y., GLASSER, F.P., Phase Relations in the System $CaO-SiO_2-H_2O$ System to 200ºC, Cement and Concrete Research **34** (2001) 1529-1534.

[22] DICKSON, C.L., BREW, D.R.M., GLASSER, F.P., Solubilities of $CaO-SiO_2-H_2O$ Phases at 25º,55ºand 85ºC, Advances in Cement Research **16** (2004) 35-43.

[23] RICHARDSON, I., VAN DAMME, H., Hydration Chemistry and Structure of Cement Systems, Paper TPL-2 (Proc. 12th. International Congress on the Chemistry of Cement, Montreal, 8-13 July 2007), Nat Res. Council of Canada (2007).

[24] SCRIVENER, K.L., KIRKPATRICK, R.J., Innovation in Use and Research on Cementitious Materials Paper MPL-2 (Proc.12th. International Congress on the Chemistry

of Cement, Montreal, 8-13 July 2007), Nat. Res. Council of Canada (2007)
[25] VERBECK, G.A., HELMUTH, R.A., Effect of Cure Temperature on Concrete Strengths (Proc. 5th Intl. Congress. on the Chemistry of Cement,Tokyo), Vol. 3 (1968) 1-32.
[26] VAN BREUGEL, K., KOENDERS, E.A.B., "Numerical Simulation of the Effect of Elevated Temperature Curing on Porosity of Cement- Based Systems", Mechanisms of Chemical Degradation of Cement- Based Systems (SCRIVENER, K.L., YOUNG, J.F., Eds) E. and F. Spon (1997) 235-242.
[27] MOURET, M., BASCOUL, A., ESCADEILLAS, G., "Influence of Elevated Aggregate Temperature on Concrete Strength", Mechanisims of Chemical Degradation of Cement-Based Systems (SCRIVENER, K.L., YOUNG, J.F., Eds), E. and F. Spon (1997) 227-234.
[28] PARROTT, L.J., An Examination of the Silicate Structure of Tricalcium Silicate Hydrated at Elevated Temperatures, Cement and Concrete Res. **11** (3) (1981) 415-420.
[29] ATKINS, M., LACHOWSKI, E.E., GLASSER, F.P., An Investigation of the Solid and Aqueous Chemistry of 10 Year Old Portland Cement With and Without Silica Modifier, Advances in Cement Research **5** (1993) 66-71.
[30] JENSEN, O.M., Autogenous Phenomena in Cement-Based Materials"(PhD Thesis, University of Aalborg, Denmark), ISBN 87-91606-00-4 (2005).
[31] BERNER, U., Evolution of Pore Water Chemistry During Degradation of Cement in a Radioactive Waste Repository Environment, Waste Management **12** (1992) 201-219.
[32] GLASSER, F.P., PEDERSEN, J., GOLDTHORPE, K., ATKINS, M., Solubility Reactions of Cement Components With NaCl solutions: 1. $Ca(OH)_2$ and C-S-H, Advances in Cement Research **17** (2005) 57-64.
[33] BALONIS, M., GLASSER, F.P., Densities of Cement Phases, Cement and Concr. Res. **39** (2009) 733-739.
[34] MATSCHEI, T., LOTHENBACH, B., GLASSER, F.P., Thermodynamic Properties of Portland Cement Hydrates in the System $CaO-Al_2O_3-CaSO_4-H_2O$, Cement and Concrete Res. **37** (10) (2007)1379-1410.
[35] DREVER, J.L., The Geochemistry of Natural Waters, Prentice- Hall, Saddle River, NJ (1997).
[36] BERNER, U.R., Thermodynamic Modelling of Cement Degradation: Impact of Redox Conditions on Radionuclide Release, Cement and Concrete Research **22** (1992) 465-475.
[37] SCRIVENER, K.L., Historical and Present Day Applications of Calcium Aluminate Cement, pp 3-23 in Calcium Aluminate Cements-2001 (Manghabhai, R.J., Glasser, F.P., Eds), Institute of Materials (London), ISBN 1-86125-142-4 (2001).
[38] Calcium Aluminate Cements- Proceedings of the Centenary Conference, (FENTIMAN, C. MANGABHAI R., SCRIVENER, K., Eds) IHS/BRE Press, Watford, UK (2008).