SKI Report 2007:32

Research

Low pH Cements

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May 2007

ISSN 1104-1374
ISRN SKI-R-07/32-SE

SKI Perspective

Background

Concrete and cement are used in constructions as well as in conditioning of waste in repositories for radioactive waste. The development of low pH cements for use in geological repositories for radioactive waste stem from concerns over the potential for deleterious effects upon the host rock and other EBS materials (notably bentonite) under the hyperalkaline conditions (pH > 12) of cement pore fluids. Low pH cement (also known as low heat cement) was developed by the cement industry for use where large masses of cement (e.g. dams) could cause problems regarding heat generated during curing. In low pH cements, the amount of cement is reduced by substitution of materials such as fly ash, blast furnace slag, silica fume, and/or non-pozzolanic silica flour.

SKB has (as the Finnish Posiva and the Japanese NUMO) defined a pH limit ≤ 11 for cement grout leachates. Because low pH cement has little, or no free portlandite, the cement consists predominantly of calcium silicate hydrate (CSH) gel with a Ca/Si ratio ≤ 0.8.

Purpose

The current project is aimed to give a detailed literature review, followed by an attempt to reproduce some experimental results of low pH cement leaching by using the current cement models (from work year 2005 and new modelling development).

Results

The principal focus for influence of hyperalcaline fluids from cement in safety assessment lies with the behaviour of bentonite. The conclusions from the literature study can be summerized:

- Low pH cements may supply approximately 50 % less hydroxyl ions than conventional OPC (ordinary portland cement) for a given volume of cement, but mass balance constraints are complicated by the uncertainty concerning the type of secondary minerals produced during cement-bentonite interaction.
- The change of aqueous speciation of silicon at pH 10 has a significant impact upon the solubility of montmorillonite and would thus constitute a logical choice of pH limit for cement-derived pore fluids, but it is unlikely that cement-based grouts could be developed to meet this limit.
- Control of mass transport by diffusion processes serves as a significant constraint over the amount of bentonite that can be degraded. Computer simulations indicate that porosity reduction is likely at the interface between cement and bentonite. However, it is not clear how the transport properties of bentonite may be modified due to mineral alteration processes.
- There are considerable uncertainties concerning the precise mechanism of the rate of montmorillonite dissolution at elevated pH. The rate of dissolution may be inhibited by the presence of dissolved Si (and perhaps Al), but this mechanism has yet to be confirmed at high pH. The type of secondary minerals assumed to form from cement-bentonite interaction will also have a significant impact upon the rate of montmorillonite dissolution.

- It is necessary to use additives such as superplasticiser to improve the workability of low-pH cements. These organic additives have the potential to complex with radionuclides and enhance their mobility. Data regarding these properties are sparse and require further investigation.

Low pH cement systems have received little attention thus far regarding the development of models for the chemical evolution of pore fluids. Low Ca/Si CSH gels show preferential leaching of Si, which is in marked contrast with gels of greater Ca/Si ratio. Models apparently capable of predicting pore fluid composition coexisting with low Ca/Si CSH gels are a modified Berner model and a solid-solution model proposed by Sugiyama and Fujita.

Effect on SKI supervisory and regulatory task

An understanding of the behaviour and influence of cement in repositories is necessary for upcoming SKI reviews of SKB reporting for repositories for low- and intermediate level waste (SFR) and spent nuclear fuel. This study will a constitute a basis for further dialogue with SKB on the use of cement in repositories and on the required knowledge base for new materials.

Project information

Responsible at SKI has been Christina Lilja

SKI reference: SKI 2006/366
Project number: 200609032

Earlier reports in this project: Benbow, S., Watson, C., and Savage, D., Investigating conceptual models for physical property couplings in solid solution models of cement, SKI Report 2005:64, Swedish Nuclear Power Inspectorate, Stockholm, November 2005.

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Summary

The development of low-pH cements for use in geological repositories for radioactive waste stems from concerns over the potential for deleterious effects upon the host rock and other EBS materials (notably bentonite) under the hyperalkaline conditions (pH > 12) of cement pore fluids. Low pH cement (also known as low heat cement) was developed by the cement industry for use where large masses of cement (e.g. dams) could cause problems regarding heat generated during curing. In low pH cements, the amount of cement is reduced by substitution of materials such as fly ash, blast furnace slag, silica fume, and/or non-pozzolanic silica flour. SKB and Posiva have ruled out the use of blast furnace slag and fly-ash and are focusing on silica fume as a blending agent. Currently, no preferred composition has been identified by these agencies.

SKB and Posiva have defined a pH limit ≤ 11 for cement grout leachates. To attain this pH, blending agents must comprise at least 50 wt % of dry materials. Because low pH cement has little, or no free portlandite, the cement consists predominantly of calcium silicate hydrate (CSH) gel with a Ca/Si ratio ≤ 0.8.

Although there are potential implications for the performance of the spent fuel and cladding due to the presence of hyperalkaline fluids from cement, the principal focus for safety assessment lies with the behaviour of bentonite. There are a number of potential constraints on the interaction of hyperalkaline cement pore fluids with bentonite, including mass balance, thermodynamic issues, mass transport, and kinetics, but none of these is likely to be limiting if conventional OPC cements are employed in repository construction. Nevertheless:

- Low-pH cements may supply approximately 50 % less hydroxyl ions than conventional OPC for a given volume of cement, but mass balance constraints are complicated by the uncertainty concerning the type of secondary minerals produced during cement-bentonite interaction.
- The change of aqueous speciation of silicon at pH 10 has a significant impact upon the solubility of montmorillonite and would thus constitute a logical choice of pH limit for cement-derived pore fluids, but it is unlikely that cement-based grouts could be developed to meet this limit.

- Control of mass transport by diffusion processes serves as a significant constraint over the amount of bentonite that can be degraded. Computer simulations indicate that porosity reduction is likely at the interface between cement and bentonite. However, it is not clear how the transport properties of bentonite may be modified due to mineral alteration processes.
- There are considerable uncertainties concerning the precise mechanism of the rate of montmorillonite dissolution at elevated pH. The rate of dissolution may be inhibited by the presence of dissolved Si (and perhaps Al), but this mechanism has yet to be confirmed at high pH. The type of secondary minerals assumed to form from cement-bentonite interaction will also have a significant impact upon the rate of montmorillonite dissolution.

Low-pH cement systems have received little attention thus far regarding the development of models for the chemical evolution of pore fluids. Low Ca/Si CSH gels show preferential leaching of Si, which is in marked contrast with gels of greater Ca/Si ratio. Models apparently capable of predicting pore fluid composition coexisting with low Ca/Si CSH gels are a modified Berner model and a solid-solution model proposed by Sugiyama and Fujita.

The solubility of silica in pore fluids coexisting with low Ca/Si gels may exceed that of amorphous silica, and may pose problems regarding the stability of montmorillonite in relation to framework silicates such as feldspars. However, the potential rate of conversion of montmorillonite to feldspar under repository conditions is uncertain.

It is necessary to use additives such as superplasticiser to improve the workability of low-pH cements. These organic additives have the potential to complex with radionuclides and enhance their mobility. Data regarding these properties are sparse and require further investigation.

Contents

1 Introduction

The development of low-pH cements for use in geological repositories for radioactive waste stems from concerns over the potential for deleterious effects upon the host rock and other EBS materials (notably bentonite) under the hyperalkaline conditions (pH > 12) of cement pore fluids, e.g. Savage (1997), Baker et al. (2002), Gaucher and Blanc (2006). Consequently, radioactive waste agencies seek an alternative to conventional OPC cements, such as 'low-pH cement'.

Low pH cement was developed by the cement industry, not for its chemical properties, but for its low heat of hydration, for use where large masses of cement (e.g. dams) could cause problems regarding heat generated during curing. This type of cement was first applied in radioactive waste studies by AECL in Canada who developed a low heat of hydration Portland cement (LHHPC) for use as a concrete plug in repository galleries (Gray and Shenton, 1998). The fundamental principle in the production of low pH cement is that the amount of cement is reduced by substitution of materials such as fly ash, blast furnace slag, silica fume, and/or non-pozzolanic silica flour. The lower cement content reduces the heat of hydration through removal of the portlandite component of the cement.

The lack of free portlandite ensures that the pH of entrained pore fluid is also reduced, from greater than 12.5 to less than 11. Because low pH cement has little, or no free portlandite, the cement consists predominantly of calcium silicate hydrate (CSH) gel. Low pH cement has a high strength and low hydraulic conductivity, making it suitable for use in the repository environment (Chandler et al., 2002), but greater proportions of silica fume may lead to slower gain of strength, lower ultimate strength, and greater sensitivity to curing conditions (Glasser, 1996).

Unfortunately, the workability of the low pH cement must be increased by the addition of additives such as superplasticiser. Although such additives may be benign in usual engineering projects, in radioactive waste disposal, their impact upon long-term mobility of radionuclides through potential complexation of radionuclides has to be assessed (see Section 4).

This report discusses the rationale for the choice of pH limits for pore fluids from cement grouts (Section 2), the types and characteristics of low pH cements (Section 3), potential problems associated with the use of additives such as superplasticisers (Section 4), and the available models for prediction of long-term chemical behaviour of low-pH cements (Section 5).

2 Rationale and safety aspects

A maximum pH of 11 has been identified as a target for low-pH grouts (Bodén and Sievänen, 2005), but the rationale for the definition of this limit is unclear. Clearly, OH^- concentrations can be expected to be reduced two orders of magnitude between pH 13 and pH 11 (from a nominal 1700 mg/l to 17 mg/l), but the pH 11 limit appears an arbitrary definition, rather than one linked to a 'function indicator' (SKB, 2004). Bodén and Sievänen (2005) state that:

> *"The use of standard cementitious material creates pulses of pH 12-13 in the leachates and release alkalis. Such a high pH is detrimental and also unnecessarily complicates the safety analysis of the repository, as the effect of a pH-plume should be considered in the evaluation. As no reliable pH-plume models exist, the use of products giving a pH below 11 in the leachates facilitates safety analysis. Also, according to current understanding, the use of low-pH cement ($pH \leq 11$) will not disturb the functioning of the bentonite, although limiting the amount of low-pH cement is recommended".*

Although there may be deleterious impacts from hyperalkaline fluids upon the performance of both the spent fuel and cladding, and the host rock, the focus adopted here is upon the performance of the bentonite buffer. It is suggested that the impact of hyperalkaline fluids could be evaluated in terms of the effect of effective clay density on clay swelling pressure. The relationship between clay dry density and the swelling pressure of MX-80 bentonite in pure water is well-defined (*Figure 1*).

It may be seen from *Figure 1* that the critical dry density for developing a swelling pressure of 1 MPa (SKB function indicator for swelling pressure) is 1000 kg m^{-3}, which is well within the overall required buffer density of 1590 kg m^{-3} (saturated density of 2000 kg m^{-3}) for other SKB function indicators, such as that to prevent colloid transport or microbial activity.

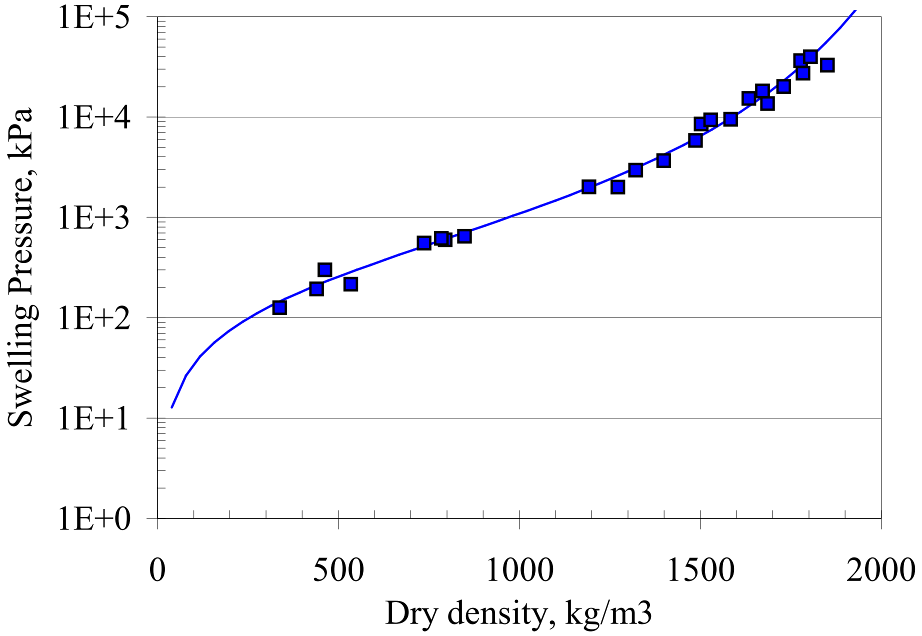

Figure 1: Relationship between swelling pressure in pure water and clay dry density. From Karnland et al. (2002).

The effect of conversion of montmorillonite to non-swelling minerals such as zeolites through interaction with hyperalkaline fluids can be investigated through the relationship between clay dry density and the fraction of non-swelling mineral (JNC, 2000):

$$\rho_b = \frac{\rho_d(1-R_s)}{1-\dfrac{\rho_d R_s}{\rho_s}} \qquad (1)$$

where ρ_b = effective clay density; ρ_d = dry density of the mixture of bentonite and non-swelling material; R_s = fraction of non-swelling mineral (e.g. zeolite); and ρ_s = grain density of non-swelling mineral.

We can use the formula to estimate the effective dry density of the clay if, for example, 10 % of the montmorillonite were converted to a non-swelling mineral such as zeolite by degradation processes. If we assume an initial porosity of 0.41, and assume that the volume vacated by the bentonite becomes occupied by zeolite with a grain density of 2200 kg m^{-3}, then the dry density of the mixture would change from an initial 1590 kg m^{-3} (pure bentonite) to 1561 kg m^{-3} (mixture of bentonite and zeolite). The resulting effective clay density would be reduced from 1590 kg m^{-3} to 1512 kg m^{-3} (equation (1)), and the swelling pressure from 10 MPa to 6 MPa (*Figure 1*). Reduction of the swelling pressure below 1.0 MPa (SKB function indicator for swelling pressure) would require the dry density of the mixture to decrease to less than 1000 kg m^{-3}, which corresponds to a loss of more than 55 % of the original montmorillonite content in this case.

2.1 Constraints on cement-bentonite interaction

Focusing upon the impact of high pH fluids on bentonite stability, there are a number of controls which need to be considered governing the destruction of bentonite due to interaction with cement (e.g. Takase, 2004):

- Mass balance (are there enough hydroxyl ions from cement/concrete to perturb bentonite stability?).
- Thermodynamic relationships (what are the differences from a thermodynamic perspective between neutral and high pH?).
- Mass transport (are degradation processes limited by the amounts of OH^- which could diffuse into the bentonite?).
- Reaction kinetics (are the rates of reaction fast enough for degradation to take place?).

These controls are discussed in the following sections.

2.1.1 Mass balance

The mass balance control focuses on the relative amounts of cement and bentonite in the near-field and the potential for destruction of bentonite properties by dissolution of montmorillonite. A simple stoichiometry for the dissolution of montmorillonite at high pH is as follows:

$$Na_{.33}Mg_{.33}Al_{1.67}Si_4O_{10}(OH)_2 + 4.68OH^- + 2H_2O \Rightarrow$$
$$0.33Na^+ + 0.33Mg^{2+} + 1.67Al(OH)_4^- + 4\ HSiO_3^- \qquad (2)$$

which implies that dissolution of one mole of montmorillonite consumes 4.68 moles of OH^-, or that approximately 13 moles of OH^- can be consumed per kg of montmorillonite

(MW montmorillonite = 367.02 g). If MX-80 bentonite contains roughly 90 wt % montmorillonite, then montmorillonite dissolution can account for 0.9 x 13 ~12 moles of OH^- per kg of (dry) bentonite. If in the KBS-3V concept compacted bentonite has a target water-saturated density of 2000 kg m^{-3} (equivalent to a clay dry density of 1590 kg m^{-3} and a porosity of 41%) (SKB, 2004), then there are approximately 3900 moles of montmorillonite in each cubic metre of bentonite, theoretically capable of neutralising 18 250 moles of OH^-.

Karlsson et al. (1999) state that there is 420 kg of hydrated Degerhamn cement paste in 1 m^3 of concrete. This amount of cement paste can liberate 8 000 moles of OH^- (from both portlandite and CSH gel leaching) (Karlsson et al., 1999). Since cement paste has a density of 2000 kg m^{-3} (Taylor, 1990), the amount of OH^- ions leachable from 1 m^3 of *cement* is theoretically 38 100 moles (2000/420 x 8000). This amount of hydroxyl ions could be titrated by complete dissolution of the montmorillonite in 2.1 m^3 of bentonite (38 100 ÷ 18 250).

SKB envisage that its spent fuel repository will require the use of 8700 tonnes of cement in shotcrete and 900 tonnes of cement in grouting (9600 tonnes total, equivalent to 4800 m^3 of cement paste). This volume of cement contains a theoretical amount of hydroxyl ions to consume 10020 m^3 of bentonite. Since there is likely to be in the order of 100 000 tonnes of dry bentonite (~60 000 m^3 of bentonite assuming a dry density of 1590 kg m^{-3}) in deposition holes in the Swedish spent fuel repository (for 9 000 tonnes of spent fuel in 4500 canisters - SKB, 2004), then in theory, 16 % of this could be destroyed by reaction with cement pore fluids.

Low-pH grout mixes using Degerhamn cement-based OPC and silica fume with an overall Ca/Si ~ 0.8 (i.e. producing a leachate pH $\leq$ 11) considered by SKB (e.g. Bodén and Sievänen, 2005), typically contain only 55 wt % OPC in the grout paste and is thus likely to produce roughly 21 000 moles of OH^- per cubic metre of grout (2000/420 x 8000 x 0.55), assuming a similar density to OPC paste. Dissolution of 60 % of the montmorillonite in 1 m^3 of bentonite would therefore require all the hydroxyl ion content from approximately 0.52 m^3 of low-pH grout.

As identified by Takase (2004) however, the mass balance issue is complicated by the nature of the potential secondary products of cement-bentonite interaction. Growth of secondary minerals will contribute to consumption or generation of OH^-, e.g. the precipitation of tobermorite:

$$5Ca^{2+} + 6HSiO_3^- + 4OH^- + 5.5H_2O \Rightarrow Ca_5Si_6H_{21}O_{27.5} \qquad (3)$$

will enhance the pH buffering capacity of the bentonite and decrease the amount of montmorillonite to be dissolved by consuming hydroxyl ions, whereas the precipitation of zeolites[1] such as analcime:

$$Na^+ + Al(OH)_4^- + 2HSiO_3^- \Rightarrow NaAlSi_2O_6 + 2OH^- + 2H_2O \qquad (4)$$

will generate OH^-, prolong the scale of the hyperalkaline alteration, and potentially increase the amount of montmorillonite dissolution.

In this regard, it is likely that there will be a difference between alteration of bentonite at pH > 12 and that at lower pHs. Mineralogical alteration at pH > 12 is dominated by the growth of calcium silicate hydrate solids, such as tobermorite (equation (3)), whereas alteration at pH < 12 is typified by zeolites, such as phillipsite, clinoptilolite, and analcime (Savage et al., 2007). Secondary mineral formation at pH < 11 (i.e. at pH conditions typical of low-pH cement) will therefore be zeolitic, and thus tend to extend the zone of alkaline alteration in accord with equation (4). The amounts and types of secondary mineral formation can thus have a profound effect upon the degree of bentonite alteration.

Minerals in the buffer material other than montmorillonite, e.g. quartz and chalcedony, can dissolve and consume OH^-, leading to decreased montmorillonite dissolution.

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[1] Analcime is technically a feldspathoid, but is here included as a zeolite.

2.1.2 Thermodynamic relationships

pH has a profound effect upon the aqueous speciation of metals and the solubilities of minerals. With regard to the stability of bentonite in alkaline fluids, the behaviour of silicon is perhaps the most important.

The variation of silicon speciation and quartz solubility with pH is shown in *Figure 2*. It may be seen from this Figure that the aqueous speciation of Si is dominated by the neutral species $SiO_{2(aq)}$ across the bulk of the pH range and the solubility of quartz is also constant across this range at 10^{-4} moles l^{-1}. Above pH 10 however, $SiO_{2(aq)}$ dissociates to produce the charged species $HSiO_3^-$. Correspondingly, the solubility of quartz (as a proxy for the solubility of silicate minerals), increases by three orders of magnitude over that observed in the pH range 1-10. At pH > 13, a second dissociation of $SiO_{2(aq)}$ occurs, such that $H_2SiO_4^{2-}$ is the stable aqueous species, accompanied by further increase in quartz solubility.

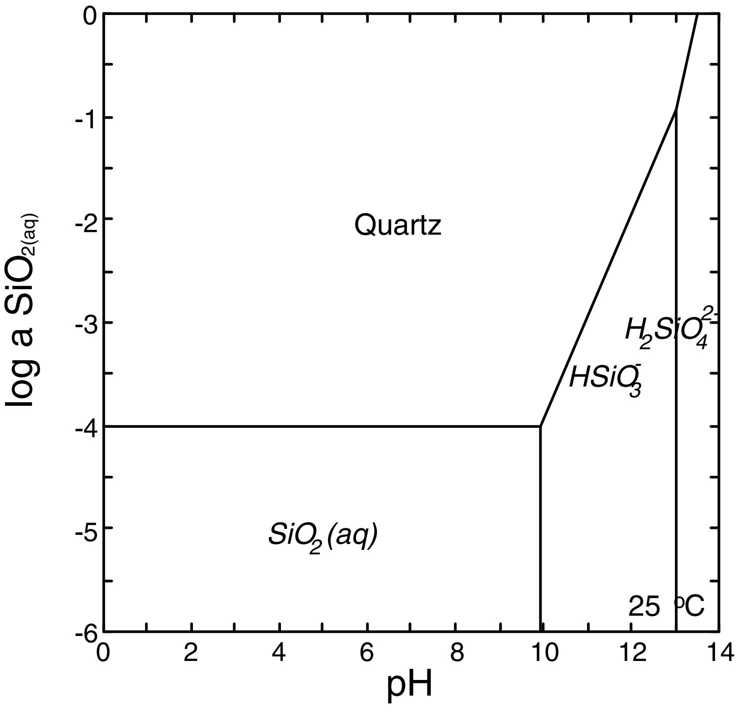

Figure 2: Variation of Si speciation and quartz solubility with pH. Calculations carried out using Geochemists Workbench (Bethke, 1996).

This change of silicon speciation (and that of Al also) with pH thus has a significant effect upon hydrolysis reactions of montmorillonite:

pH < 10: $Na_{.33}Mg_{.33}Al_{1.67}Si_4O_{10}(OH)_2 + 2H_2O \Rightarrow$

$$0.33Na^+ + 0.33Mg^{2+} + 1.67Al^{3+} + 4SiO_{2(aq)} + 6OH- \quad (5)$$

10 < pH < 13: $Na_{.33}Mg_{.33}Al_{1.67}Si_4O_{10}(OH)_2 + 4.68OH^- + 2H_2O \Rightarrow$

$$0.33Na^+ + 0.33Mg^{2+} + 1.67Al(OH)_4^- + 4HSiO_3^- \quad (6)$$

pH > 13: $Na_{.33}Mg_{.33}Al_{1.67}Si_4O_{10}(OH)_2 + 8.68OH^- + 2H_2O \Rightarrow$

$$0.33Na^+ + 0.33Mg^{2+} + 1.67Al(OH)_4^- + 4H_2SiO_4^{2-} \quad (7)$$

At pH < 10, dissolution of each mole of montmorillonite effectively generates six hydroxyl ions, whereas the amount of hydroxyl ions consumed increases from 4.68 at 10 < pH < 13, to 8.68 at pH > 13.

Returning to the issue of defining limits for pH for bentonite stability, it may be concluded that from a perspective of thermodynamics, a critical boundary occurs at pH 10, where there is a substantial change in the aqueous speciation of silicon.

2.1.3 Mass transport

Cement grouts may not be located adjacent or near to bentonite in deposition holes, so that hydroxyl ions may be neutralised by reaction with bicarbonate ions in groundwater or with host rock minerals before the bentonite buffer is contacted by cement pore fluids along groundwater flow paths. These scenarios have been investigated by Vieno et al. (2003) with regard to migration of cement pore fluids at ONKALO with the conclusion that cement pore fluids were unlikely to impair the performance of bentonite in waste package deposition holes.

During resaturation, bentonite may be improperly swollen, hence cement grout water may flow over the bentonite surface and erode it, rather than diffuse inwards. Moreover, water derived from cement grout could be involved in the initial resaturation of the bentonite, leading to alkaline attack at an early stage of the buffer evolution.

If cement pore fluids do contact the bentonite buffer, reaction will be limited by slow diffusive transfer of hydroxyl ions into the bentonite. Effective diffusion coefficients for solute transport though bentonite are very low, and generally less than 10^{-10} m^2 s^{-1}. Mass transport by diffusion will thus inhibit alkaline alteration of bentonite.

Consideration of Fick's first law demonstrates that the magnitude of mass transfer by diffusion is dependent upon the concentration difference across the medium concerned:

$$F = -D\frac{dC}{dx} \tag{8}$$

where F = mass flux (mass of solute per unit area per unit time); D is the diffusion coefficient (area per unit time); and dC/dx is the concentration gradient.

Use of low-pH cements with entrained fluids of pH ≤ 11 could thus decrease diffusive transport of hydroxyl ions by two orders of magnitude in comparison with fluids leached from OPC cement and concrete (pH ~ 13) because of the relative differences in hydroxyl ion concentrations in pore fluids associated with the two types of grout.

Dissolution of montmorillonite constrained by the transport of OH^- ions in and around the buffer material can be simulated by combining mass transport equations with a number of mineral reactions including montmorillonite, and associated secondary phases. Using kinetic descriptions of montmorillonite dissolution and secondary mineral growth, Savage et al. (2002) noted destruction of montmorillonite over a distance of ~ 60 cm (of a 1 m length of bentonite) at pH 13 after 1000 years, but a distance of only ~10 cm after 3200 years at pH 11.3.

Simulations of cement-clay interaction generally predict porosity decreases in the clay accompanying alteration (e.g. Savage et al., 2002; Gaucher et al., 2004), which would be expected to decrease the rate of mass transport. However, this assumption is dependent upon mass transfer occurring by diffusion through the altered bentonite region, where information regarding physical properties is uncertain. For example, if cracking accompanies bentonite alteration (e.g. by zeolitisation), advective transport may be initiated, leading to more rapid transport of hydroxyl ions.

Previous experimental studies (e.g. Jefferies et al., 1988) suggest that dissolution of clay coupled with precipitation of secondary minerals can result in a net decrease, not only in porosity, but also effective diffusion coefficient, and hydraulic conductivity. However it is likely that the secondary minerals observed over such short experimental timescales will be slowly transformed into more stable minerals with time, so it is difficult to justify the assumption of diffusive transport through the altered bentonite region over much longer timescales.

2.1.4 Kinetics

The dissolution rates of most aluminosilicate minerals are accelerated by increasing OH^- concentrations at $pH > 8$ (e.g. Lasaga, 1984). A number of studies of montmorillonite dissolution at alkaline pH have been carried out in recent years. The results of these studies are summarised in *Figure 3.*

Although the data in *Figure 3* show considerable scatter (data from experiments in the temperature range 20-80 °C are covered), reaction rates are slow, being in the order of 10^{-12} mol m^{-2} s^{-1} at 25 °C under far-from-equilibrium conditions. It may be seen that there is a significant dependence upon pH (OH^-), broadly described by rate being proportional to $[H^+]^{-0.3}$. This implies that the rate of dissolution of montmorillonite is a factor of 8 greater at pH 11 than at pH 8 (ambient pH of bentonite pore fluids) and a factor of 30 greater at pH 13 than at pH 8.

In gross terms, if the rate of dissolution at pH 8 is 10^{-12} mol m^{-2} s^{-1}, then this implies that 0.23 moles of montmorillonite could be dissolved per year through interaction with pore fluid (MW of montmorillonite is 367.02 g and a typical surface area is 20 m^2 g^{-1}). Dissolution of one cubic metre of bentonite (containing 4330 moles of montmorillonite) would thus require ~20 000 years at pH 8. The measured dependence of rate upon OH^- concentration implies that ~2500 years would be required at pH 11, and only ~600 years at pH 13. This suggests that kinetics would not be a limiting constraint upon montmorillonite dissolution at elevated pH.

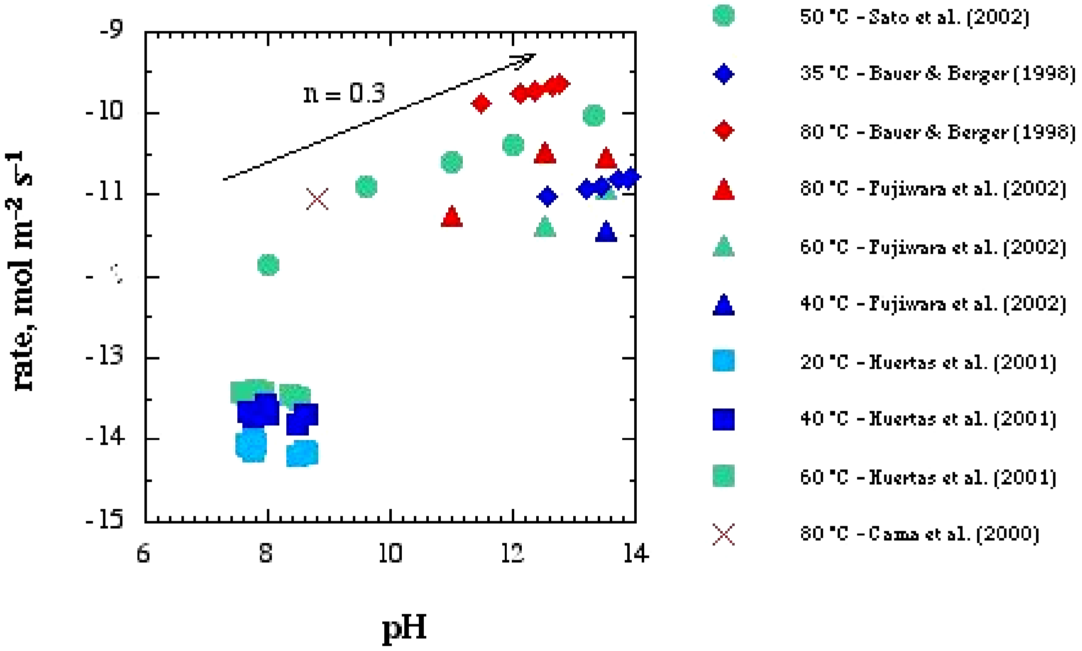

Figure 3: Summary of experimental studies of montmorillonite dissolution at alkaline pH and far-from-equilibrium conditions. Data from Bauer and Berger (1998), Cama et al. (2000), Huertas et al. (2001), Fujiwara et al. (2002), and Sato et al. (2002).

However, this is a worst-case scenario, i.e. that dissolution of montmorillonite occurs under far-from-equilibrium conditions. In reality, the rate of dissolution would be slowed by approach to equilibrium, although the precise mechanism of montmorillonite dissolution close to equilibrium is uncertain. For example, Cama et al. (2000) identified both transition-state theory (TST) and Si-inhibition mechanisms which could describe their experimental data near equilibrium. Application of these models to define montmorillonite dissolution over long timescales produces dramatically different results, with the TST model producing much greater montmorillonite dissolution (Takase, 2004). For example, the Si-inhibition model with a Si concentration of 10^{-3} moles l^{-1} may reduce the dissolution rate of montmorillonite by three orders of magnitude over that measured in Si-free systems (*Figure 4*). However, since Cama et al. (2000) conducted their experiments at pH 8.8 only, currently it is not clear if the Si-inhibition mechanism is appropriate at pH > 10, where aqueous speciation of silicon changes markedly. Montmorillonite dissolution could be further inhibited by Al dissolved in the pore fluid as suggested for other clay minerals such as kaolinite (Oelkers et al., 2001), but this issue is as yet, uninvestigated for montmorillonite.

Consequently, there are major uncertainties regarding the application of a reliable kinetic model for montmorillonite behaviour over the long-term.

Also, Oda et al. (2004) has shown that assumptions concerning the stability of potential secondary minerals can have a dramatic effect upon the saturation state of montorillonite in alkaline fluids, and hence the overall montmorillonite dissolution rate. The choice of secondary minerals in predictive calculations must therefore be chosen with care (e.g. Savage et al., 2007), since a method allowing the computer code to select the most thermodynamically-stable phase can lead to unrealistic choices of secondary minerals, because of control of mineral growth through kinetics and Ostwald step processes (Dibble and Tiller, 1981; Steefel and Van Cappellen, 1990).

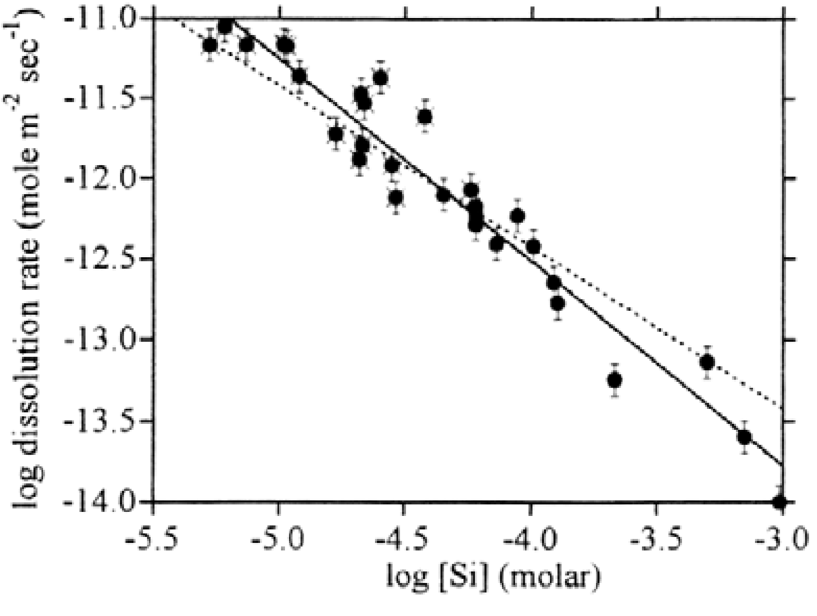

Figure 4: Effect of dissolved silicon concentration on montmorillonite dissolution rate at pH 8.8 and 80 °C. From Cama et al. (2000).

2.2 Discussion

It is apparent from the above evidence that it is not possible to rule out deleterious effects of the presence of OPC cements upon bentonite stability from perspectives of mass balance, thermodynamics, mass transport, or kinetics:

- Mass balance constraints are complicated by the uncertainty concerning the type of secondary minerals produced during cement-bentonite interaction.
- The change of aqueous speciation of silicon at pH 10 has a significant impact upon the solubility of montmorillonite and would thus constitute a more rational choice of pH limit for cement-derived pore fluids, but it is unlikely that cement-based grouts could be developed to meet this limit.
- Control of mass transport by diffusion processes serves as a significant control over the amount of bentonite that can be degraded. Computer simulations indicate that porosity reduction is likely at the interface between cement bentonite. However, it is not clear how the properties of bentonite may be modified due to mineral alteration processes. If fracturing accompanies alteration, then rates of mass transport may be increased.
- There are considerable uncertainties concerning the precise mechanism of montmorillonite dissolution at elevated pH. The rate of dissolution may be inhibited by the presence of dissolved Si (and perhaps Al), but this mechanism has yet to be confirmed at high pH. The type of secondary minerals assumed to form from cement-bentonite interaction will also have a significant impact upon the rate of montmorillonite dissolution.

3 Characteristics of low-pH cement

Glasser (1996) noted that the impact of adding blending agents such as silica fume to cement is two-fold:

- the resulting solid hydrates are chemically modified and develop increased sorption for alkalis relative to OPC.
- the reaction between portlandite and silica fume impacts upon the presence of portlandite itself, but significant proportions of silica may be necessary to use up all the available portlandite (generally in excess of 20 wt %).

The best-characterised blending agents are blast furnace slag and fly ash (Glasser, 1996). Blast furnace slag is generally composed of CaO, MgO, Al_2O_3, and SiO_2, with smaller amounts of iron oxide, TiO_2, Na_2O, and K_2O. The reactivity in the cement system is due to its high glass content. Glasser (1996) describes a reaction scheme for all these glassy materials where Si-OH-Si bonds in the glass are hydrolysed by OH^- in the cement solution. Fly ash can be variable in composition and some may have high CaO, MgO, and Al_2O_3 contents which may cause delayed expansion (Glasser, 1996).

Silica fume appears to be the most promising blending agent for repository low-pH grouts (Bodén and Sievänen, 2005). Silica fume is a by-product of electrothermal ferrosilicon production, so its sources are limited to those areas where electricity is cheap (Glasser, 1996). Its availability is restricted by demand for the principal product (ferrosilicon). The fine particle size of silica fume can lead to difficulties in practice – issues include problems achieving physical mixing without agglomeration, unfavourable mix rheology, and excessive shrinkage in immediate post-setting stage (Glasser, 1996). However, silica fume-OPC blends can achieve high compressive strengths and low permeabilities.

3.1 Chemical properties

The principal solid phase in low-pH cement is a low Ca/Si (< 1.0) CSH gel. Production of low Ca/Si CSH gel increases the average size of the silicate anions it contains, with a similar effect to that of carbonation (Taylor, 1993). Reaction with pozzolans also tends to increase the Al/Ca ratio of the CSH. With microsilica as the additive, the mean Ca/Si ratio remains at about 1.5 for as long as any portlandite remains. If all the $Ca(OH)_2$ is consumed, then the Ca/Si ratio falls to around 1.0. A ^{29}Si NMR study showed that the addition of silica fume increased the rate of polymerisation of CSH gel – for a C_3S paste at an age of 28 days, the mean chain length was 2.6 in the absence of silica fume, and 3.6 if the latter was present (Taylor, 1993). In general, the decrease in Ca/Si ratio of CSH gel might occur by either (Taylor, 1993):

- addition of silicate tetrahedra to existing chains; and/or
- formation of new silicate chains.

This implies that there are increased proportions of tobermorite-type regions in CSH gel and that there is an increase in chain length associated with decreasing Ca/Si ratio.

A number of studies have shown that the addition of silica fume greatly accelerates the hydration of C_3S and that the CSH gel thus formed is highly polymerised, e.g. Groves and Rodger (1989). Groves and Rodger (1989) noted excellent bonding between the CSH gel and residual silica which suggests that such a system may be capable of developing high strength.

3.1.1 Interaction with groundwater

Harris et al. (2002) have published experimental data describing the leaching of CSH gels of variable Ca/Si ratio in pure water under both 'static' and 'sequential' leaching conditions. Results of some of their experiments are shown in Figure 5. It may be seen from Figure 5 that to achieve a pH less than 11, then the CSH gel must have a Ca/Si ratio less than 0.81. Unlike gels with a greater Ca/Si ratio, gels of Ca/Si ≤ 0.81 do not show dramatic incongruent dissolution behaviour. In other words, leaching of these gels produces a fluid with a broadly constant Ca/Si ratio with time/volume throughput (Figure 6).

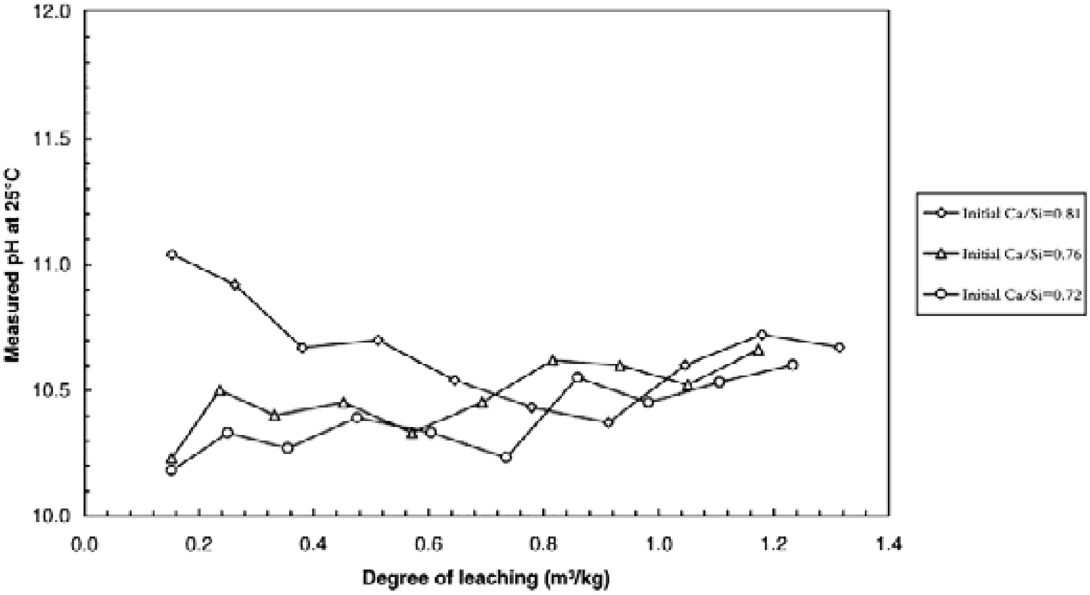

Figure 5 Variation of pH during leaching of CSH gels of variable Ca/Si ratio in pure water. From Harris et al. (2002).

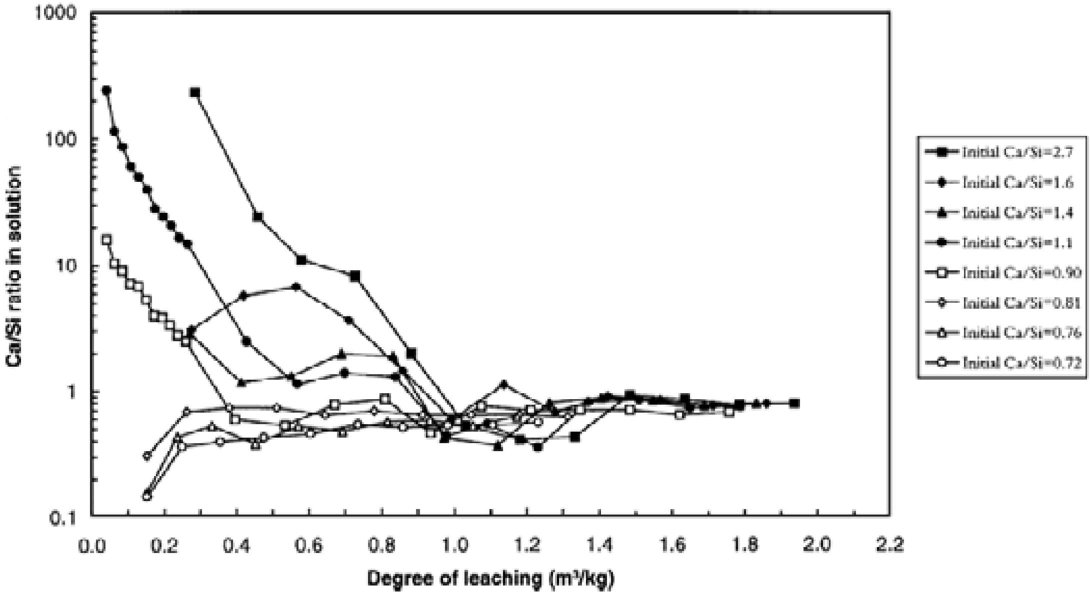

Figure 6 Variation of Ca/Si ratio in solution during leaching of synthetic CSH gels in pure water. From Harris et al. (2002).

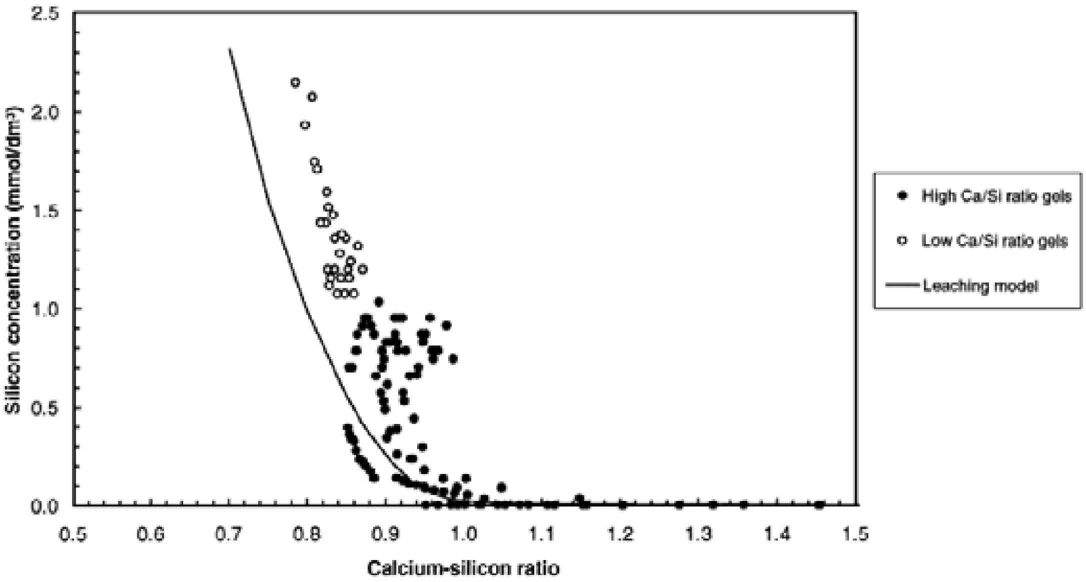

Figure 7 Evolution of silicon concentration during the leaching of CSH gels. From Harris et al. (2002). The line is derived from the amended Berner model.

Unlike the higher Ca/Si ratio gels, those with Ca/Si ≤ 0.81 show a Ca/Si ratio decreasing towards unity as leaching proceeds. This implies preferential leaching of silica from the gel, which contrasts with gels of higher Ca/Si ratio which show the preferential removal of Ca. A high silica solubility is also associated with gels of lower Ca/Si ratio (Figure 7). Harris et al. (2002) modelled their experimental data for gels with Ca/Si ≤ 1 using the Berner model (Berner, 1988), with the following solids and solubility constants:

$$\mathrm{SiO_2}, \log K = -0.471 + \frac{1.301}{\mathrm{Ca/Si} - 1.024}$$

$$\mathrm{CaH_2SiO_4}, \log K = -9.59 - \frac{0.024}{\mathrm{Ca/Si} - 1.025}$$

This model seems to reproduce experimental data for pH reasonably well, but less so for silicon (*Figure 7*).

The leaching behaviour of low pH cement has been investigated by Owada et al. (1999). The cement concerned was a so-called ‘HFSC’ (high fly ash silica fume cement). The cement composition was modelled using assumptions defined by Berner (Berner, 1992), and the interaction with water was modelled using solubility constants also defined by

Berner (Berner, 1992). Unlike Harris et al. (2002), Owada et al. (1999) did not adjust the parameters of the Berner model to account for the low Ca/Si ratio of the HFSC cement, so that their model extrapolations tended to overestimate the pH of the pore fluid at high degrees of leaching. However, Owada et al. (1999) attributed these discrepancies to the behaviour of aluminium and its potential substitution for Ca in CSH gel, rather than inadequate parameterisation of the Berner model.

Sugiyama and Fujita (2005) have developed a model for calcium silicate hydrate gel which involves a solid solution across a broad range of Ca/Si, from 0 to 2.5. The model assumes a binary non-ideal solid solution of $Ca(OH)_2$ and SiO_2 across the whole range of Ca/Si investigated. Due to this choice of end members, any Ca/Si ratio can be considered in the model. To summarise the approach, the excess energy is expressed as a sum of contributions from each end member, each expressed using a Guggenheim polynomial of order 2. The excess energy is used to derive an activity coefficient for each end-member which is then fitted to existing experimental data at a range of Ca/Si ratios. To calculate the fit, Sugiyama and Fujita split the available data into two sets corresponding to data for Ca/Si ratios less than 0.833 and greater than 0.833 (0.833 is the Ca/Si ratio of tobermorite) and performed a least-squares fit of both sets of data to obtain solid activity coefficient curves in each Ca/Si region. Furthermore, the authors argue that for Ca/Si ratios below 0.461 it is appropriate to assume that the activity of the silica end-member is unity since the solid composition at such low Ca/Si ratios is close to that of amorphous silica. Similarly, for Ca/Si ratios above 1.755, Sugiyama and Fujita argue that pure $Ca(OH)_2$ separates from the solid-solution and coexists with CSH gel, hence above this limit it is appropriate to treat each end member separately as a pure solid.

The activity coefficient of portlandite predicted by Sugiyama and Fujita's model is shown in *Figure 8*. Also marked are the interval boundaries at Ca/Si = 0.833 (tobermorite) and Ca/Si = 1.755 (portlandite co-existence). The portlandite activities that are predicted by the model are shown in *Figure 9* for a range of Ca/Si ratios. The Figure also shows the activities predicted by the solid-solution model of Börjesson (1997). The Börjesson model can only be applied to cases where Ca/Si > 1. Also

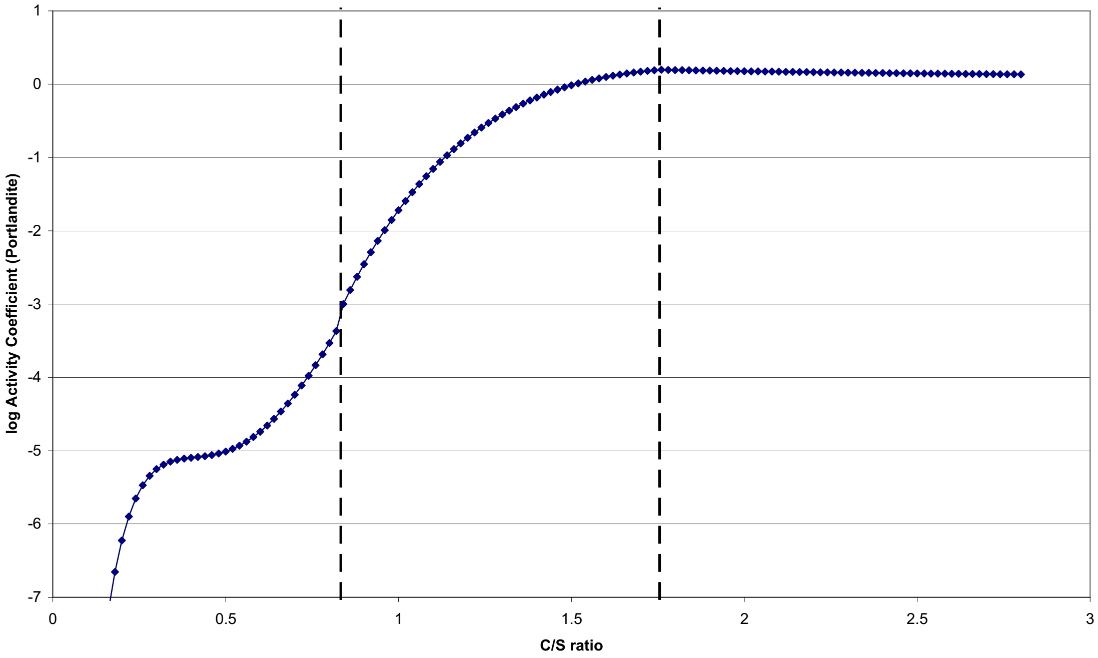

Figure 8: Sugiyama and Fujita's model for the activity coefficient of portlandite.

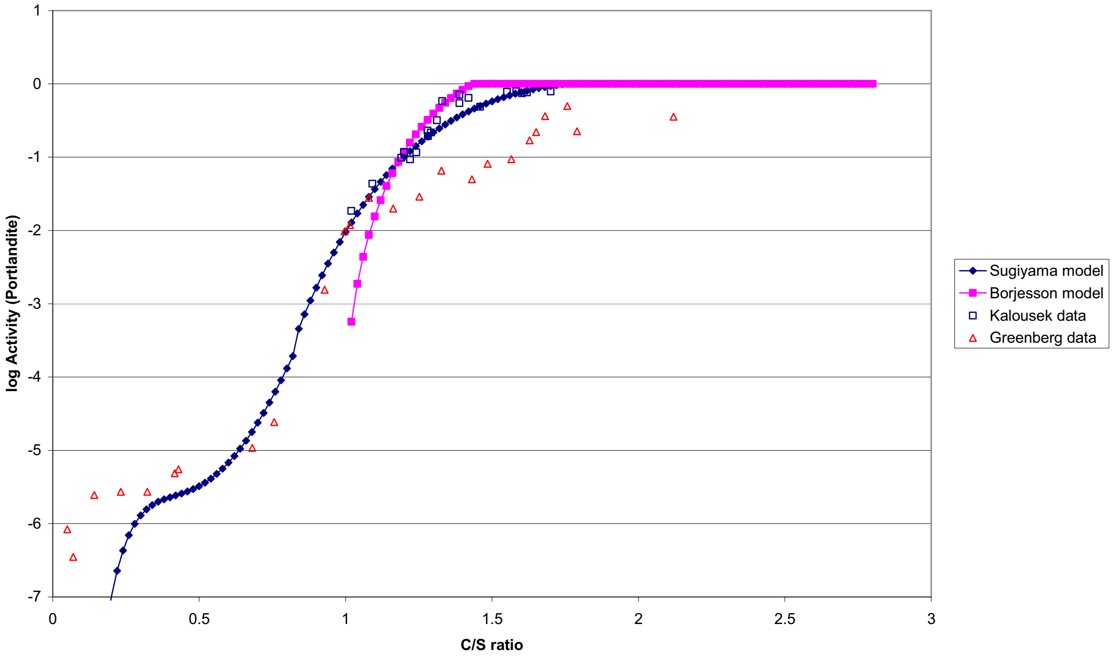

Figure 9: Portlandite activity predicted by several solid solution models together with some of the data used for fitting.

shown in the Figure are some of the data sets that were used to perform the fitting exercises for both models.

The dataset of Greenberg and Chang (1965) is one of the four datasets (which included that of Kalousek, 1952) that was used to fit Sugiyama and Fujita's model. It should be noted that the Greenberg dataset generally gives the lowest activities at Ca/Si > 1 of the datasets that were used, hence the poor fit for Ca/Si > 1, but is the only dataset that contained measurements for Ca/Si < 0.5.

Although the model of Sugiyama and Fujita provides a satisfactory fit to available experimental data, the model is somewhat unsatisfactory in that there is no microstructural evidence for any solid-solution between calcium hydroxide and silica. The model is thus more of a mathematical convenience rather than one with any physical meaning.

Saito and Deguchi (2000) investigated changes in physical properties after cement leaching and noted that admixtures such as blast furnace slag and silica fume produced a concrete which resisted leaching and showed only a small loss of performance after leaching. The pore volume in cements with pozzolanic admixtures increased by about 40-50 % after leaching, but was less than those in cements without admixtures.

Fujita et al. (2003) investigated the generation of colloids through leaching of high fly-ash and silica fume-content cement specimens with low-salinity groundwater at 20 and 60 °C for 2 and 8 months. Colloid concentrations were in the range 10^{11} – 10^{12} particles per litre with a mean particle size less than 100 nm.

3.2 Effect of Si upon bentonite stability

Consideration of *Figure 7* shows that low-pH cement grouts produce pore fluids relatively rich in Si, compared with natural groundwaters. The concentrations of Si measured by Harris et al. (2002) in CSH gel leaching experiments were up to 2.2 mmol/l, which is equivalent to the solubility of amorphous silica at neutral pH at 25 °C.

Most natural groundwaters contain Si contents equivalent to that of chalcedony (0.2 mmol/l at 25 °C) or quartz (0.1 mmol/l). Potentially, the higher Si concentrations associated with low-pH grout pore fluids could destabilise montmorillonite.

Figure 10 shows that higher Si concentrations could theoretically destabilise montmorillonite relative to Na-feldspar (albite), but the potential rate of conversion is unknown. The rate of zeolite[2] growth has been shown to depend upon hydroxyl ion concentration. For example, Hayhurst and Sand (1977) investigated experimental growth of Na, K phillipsites in the temperature range 25 – 175 °C and observed that both the rate of nucleation and the rate of growth of phillipsite increased as the

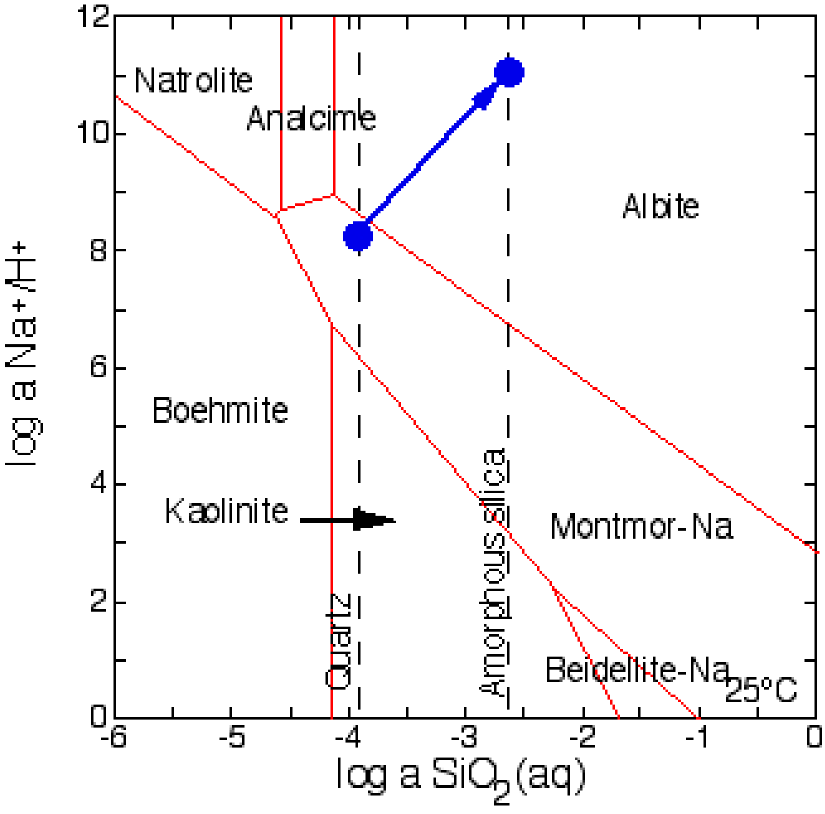

Figure 10: Activity diagram in the system NaO-MgO-Al_2O_3-SiO_2-H_2O. Mg solubility is defined by Ca-montmorillonite. The transition from ambient bentonite pore fluids saturated with typical low-salinity groundwater (Na = 250 mg/l) and quartz at pH 8.5 to those saturated with amorphous silica at pH 11 is shown by the blue arrow. Diagram constructed using Geochemists Workbench (Bethke, 1996).

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[2] Zeolites are framework silicates similar to feldspars.

concentration of OH^- ions increased, such that the rates were found to be second-order (parabolic) with respect to this component.

Further work (laboratory and natural systems) could be warranted to investigate this issue in more detail.

3.3 Work by SKB and Posiva

In their recent work to develop a low-pH cement for use in HLW repositories, SKB and Posiva evaluated the following grout compositions (Bodén and Sievänen, 2005):

- OPC + silica fume;
- OPC + blast furnace slag;
- 'super sulphate cement' (a blast furnace slag-based system + OPC + gypsum);
- 'low alkali cement' (developed by NUMO in Japan);
- OPC + fly ash.

The latter system (OPC + fly ash) was dropped early in the trials due to problems relating to the availability and stability of the raw materials. After a pilot test, blast furnace slag was also ruled out due to the high leaching of sulphide, which has potential consequences for the enhanced corrosion of copper (Bodén and Sievänen, 2005). The Japanese 'low alkali cement' was also rejected due to poor penetrability in a field test. From various laboratory and field tests, Bodén and Sievänen (2005) concluded that OPC requires at least 50 weight percent of blending agents, with a Ca/Si ratio less than 0.8 to be able to maintain pH less than 11 in pore fluid leachates.

In the grout development tests, no portlandite was present in the candidate cement pastes, so that CSH gel was the main hydration product (Bodén and Sievänen, 2005). Ca remained the main alkaline component released in leaching tests. However, it was noted that the grout leachates showed increased Si concentrations, with the potential for impact upon bentonite stability.

SKB and Posiva have also started to evaluate non-cementitious materials (e.g. silica sols) as grouts for fine fractures (Bodén and Sievänen, 2005). Although silica sols seem to be likely candidates for grouting purposes, a survey of the behaviour of periclase (MgO) has suggested that this compound would not be suitable (Bodén and Sievänen, 2005).

Sievänen et al. (2005) report progress on field testing of low-pH cement grouts for larger rock fractures (> 100 μm). Field testing of grouting of finer fractures (< 100 μm) are to be conducted in Sweden. In the first pilot test, carried out in a tunnel in Helsinki, both OPC-silica and blast furnace slag–based grouts were tested. The conclusions from this test were that penetration of the grouts was good, but fluidity and strength development were unsatisfactory. Decreasing the water/solid ratio was suggested as a solution to the problem, with addition of superplasticiser. The further testing of the blast furnace slag mix was ruled out due to generation of undesirable amounts of sulphide in the pore fluid. The second pilot test involved the OPC-silica formulation only. Several formulations were evaluated in mixing tests and one was selected for a field test in the ONKALO access tunnel. However, the penetration, fluidity, and strength development were not satisfactory in comparison with an ordinary OPC mix. Differences were attributed to the very high content of silica in the low-pH formulation.

4 Effect of additives

It will be necessary to use additives in low-pH cements to improve workability and/or setting times. From the perspective of the use of cements in facilities for waste isolation, additives are organic compounds which may complex with radionuclides. Although additives are used in small amounts (approximately 1 %), the large volumes of concrete in a waste repository may mean that such organics are significant for radionuclide complexation and migration.

Superplasticisers are very high molecular weight polymers (10^4-10^5 times greater than a water molecule) which when added to a concrete mix, are adsorbed onto cement particles making them mutually repulsive or colloidal (Uchikawa et al., 1997). Onofrei et al. (1991) noted that superplasticisers preferentially sorbed onto hydrated cement phases such as tricalcium aluminium hydrate and tricalcium silicate. This behaviour releases the water, which is normally held within agglomerates of cement grains and frees it for the hydration of cement grains. Because the additive-coated cement particles are homogeneously distributed in the water phase, the amount of water available for cement hydration is increased, since fewer network voids trap water molecules. The adsorbed superplasticiser reduces the friction between each cement particle and has a smoothing effect also, allowing them to move more freely. These mixes behave as non-Newtonian fluids, enabling them to be more easily pumped and allowing emplacement of greater volumes of cement. Normally, the effects of the superplasticising agents wear off after a period of 90-120 minutes.

Superplasticisers are commercial products so that precise chemical compositions and structures are often proprietary. However, there are 4 main types:

- sulphonated naphthalene formaldehyde condensates (NS).
- sulphonated melamine formaldehyde condensates (MS).
- modified lignosulphates (LS).
- polycarboxylic acids (PC).

The first two types are the most widely used and are usually available in the form of their sodium salt.

The potential metal complexation effects of superplasticisers have been investigated by Glaus and Van Loon (2004) who selected a few concrete admixtures, such as sulphonated naphthalene-formaldehyde condensates, lignosulphonates, and a plasticiser used at the Paul Scherrer Institute for waste conditioning. The effect of these concrete admixtures on the sorption properties of Ni(II), Eu(III) and Th(IV) on cement was investigated using crushed hardened cement paste (HCP) and cement pastes prepared in the presence of these concrete admixtures. They noted that naphthalene sulphonate (NS) and polycarboxylate (PC) superplasticisers only marginally reduced Eu sorption on cement (90-95 % of that without any additive), whereas melamine sulphonate (MS) and lignosulphonate (LS) were considerably worse (65 % for MS, < 5 % for LS). Although some of the concrete admixtures investigated were shown to be strong complexants, no adverse effect on the sorption of the radionuclides tested could be observed under realistic conditions, i.e. at representative crushed hardened cement paste to pore water ratios and representative concrete admixture to cement ratios. Glaus and Van Loon (2004) concluded that sulphonated naphthalene formaldehyde condensate-type superplasticisers will not complex radionuclides significantly within the range of pore water concentrations measured. In the case of modified lignosulphates, the situation was more complicated. Modified lignosulphates would be expected to have a mobilising effect on Eu(III) with respect to solubility and sorption and, due to the analogy of Eu(III) with other trivalent lanthanides and actinides, also on these types of radionuclides.

4.1 Leachability

The principal uncertainty with regard to long-term safety is how much superplasticiser can be leached from the cement under disposal conditions.

Onofrei et al. (1991) carried out experiments to investigate the leachability of superplasticiser in cured cements. These experiments showed that naphthalene sulphonate formaldehyde condensate superplasticiser could be leached from hardened grouts, but cumulative amounts were very small ($\sim 10^{-16}$ kg m^{-2}).

Bradbury and Van Loon (1998) estimated the likely amount of superplasticiser in cement pore fluids using Na-gluconate as being typical of such compounds. Assuming a molecular weight of 196 g mol^{-1} for Na-gluconate, and a 1 wt. % concentration of additive in cement, they calculate that 31 moles of Na-gluconate would be present in a notional 1 m^3 of repository volume (assuming a 10 % cement porosity). They estimate the likely concentration of Na-gluconate in the pore fluid would be $3x10^{-5}$ M. This concentration is much less than that used in experimental studies of solubility and sorption.

Available experimental and modelling data for additive leaching therefore suggest that additive concentrations in pore fluids in hardened cement pastes are likely to be less than 10^{-5} M.

4.2 Superplasticisers used by SKB

As yet, no decision has been made by SKB regarding low-pH grout compositions or the type of superplasticiser to be used in conjunction with the grout. However, the work by Bodén and Sievänen (2005) reports the use of ‘SP40’ which is a sulphonated melamine formaldehyde condensate-type superplasticiser commonly used in cement and concrete technology.

5 Models of low-pH cement behaviour

In this section we investigate the relevance of existing models of cement to be used to model low pH cement environments. Not all cement models are applicable to modelling low pH systems, since in these systems the Ca/Si is usually less than 1. Some cement models using solid-solution models for CSH gel (e.g. Börjesson, 1997; Walker, 2003) assume $Ca(OH)_2$ and CaH_2SiO_4 end-members in the cement. For this choice of end-members the minimum possible Ca/Si ratio is 1 because both end-members contain calcium. The Sugiyama and Fujita model (2005) also involves solid-solutions, but with $Ca(OH)_2$ and SiO_2 as end-members, so can potentially represent cases when Ca/Si < 1. Thus the modelling in this section is based on the Sugiyama and Fujita model, together with experimental data from Owada et al. (1999).

5.1 Cement model

The system modelled is that used in the experiments described by Owada et al. (1999) with a 'High Fly-ash Silica Fume' Cement (HFSC) developed by JNC and Obayashi in Japan (Mihara, 1998). This cement has a Ca/Si ratio of 0.83 and a pore water pH in the range 10.3-11. The content of HFSC is given in

Table 1. Owada et al. (1999) based their cement composition on that defined by Berner (Berner, 1992) and assumed that sulphate is located in Aft (ettringite), Al and Fe are in C_3AH_6 and C_3FH_6 respectively, and that any remaining Ca and Si form CSH gel. The resulting initial mineralogy to represent the system was calculated by Owada et al. (1999) to be that shown in *Table 2*. In this Table, the amounts have been converted from the original units of mol/box (which were used as input to the chemical modelling code, SANTA CHEM (Neall et al., 2000)) to equivalent mol/m^3. *Table 3* shows the equivalent initial mineralogy when representing CSH by the two end members portlandite and SiO_2. The conversion was performed by calculating equivalent portlandite and SiO_2 amounts to give the same weight as the Owada model whilst maintaining a C/S ratio of 0.83.

Table 1: Content of HFSC assumed in Owada et al. (1999).

Constituent	**Content (wt %)**
Portland cement	40
Silica fume	20
Fly-ash	40

Table 2: Initial mineralogy in the Owada model.

Mineral	**Amount (mol/m^3)**
CSH	4.96×10^{2}
Aft (Ettringite)	3.51×10^{-1}
Quartz	4.86×10^{2}
Porosity	0.82

Table 3: Equivalent initial mineralogy in the Sugiyama and Fujita model.

Mineral	**Amount (mol/m^3)**
Portlandite	2.60×10^{3}
SiO_2	3.13×10^{3}
Aft (Ettringite)	3.51×10^{-1}
Quartz	4.86×10^{2}
Porosity	0.82

Table 4: Thermodynamic data for the minerals in the model.

Mineral	**Reaction**	**Log K (at 20°C)**
Portlandite	$\text{Portlandite} + 2H^{+} = Ca^{2+} + 2\,H_2O$	Calculated using solid solution model
SiO_2(CSH)	$SiO_2(CSH) = H_4SiO_4$	Calculated using solid solution model
Ettringite	$\text{Ettringite} + 4H^{+} = 6\,Ca^{2+} + 2Al(OH)_4^{-} + 3SO_4^{2-} + 30\,H_2O$	13.35
Quartz	$\text{Quartz} = H_4SiO_4$	-3.78
Calcite	$\text{Calcite} = Ca^{2+} + CO_3^{2-}$	-8.46
Gibbsite	$\text{Gibbsite} + H_2O = H + Al(OH)_4^{-}$	-14.91

Owada et al. (1999) considered calcite and gibbsite to be the potential secondary minerals in the system. Thermodynamic data for these and the primary minerals are given in *Table 4*. All minerals other than CSH are modelled using a simple transition state theory reaction with the reaction rate sufficiently fast as to mimic instantaneous equilibrium conditions.

The experimental set-up comprised a closed vessel in which synthetic groundwater is equilibrated with a cement sample. After equilibration, the leachate is filtered out and analysed. The vessel is then re-filled with more synthetic groundwater and the process repeated until the cement sample is totally dissolved. The composition of the synthetic groundwater is shown in *Table 5*.

Owada et al. (1999) used the SANTA-CHEM code (Neall et al., 2000) to model the system based on the Berner model. We use Quintessa's Raiden-3 code to model the solid solution based model of the system. Raiden is a geochemical transport code designed to model fully-coupled flow and transport in geochemically evolving regions. Raiden has recently been used to apply the solid solution model of Börjesson (1997) to simulate the coupling between the chemical and physical degradation of cements (Benbow et al., 2005). Since Raiden is a continuous time model, to model a leaching experiment it is necessary to impose an equivalent flow rate across the closed vessel to give rise to the same net rate of extraction of fluid from the box. The properties of the compartment used to simulate the closed vessel are given in *Table 6.*

Table 5: Chemical composition of the synthetic groundwater.

Element	**Concentration (mol/l)**
Ca	1.07×10^{-4}
Na	3.49×10^{-3}
K	6.07×10^{-5}
Al	3.48×10^{-7}
Si	3.47×10^{-4}
C	3.11×10^{-3}
S	1.25×10^{-4}
pH	8.47

Table 6: Properties of the compartment representing the closed vessel.

Property	**Value**
Solid/Liquid ratio	5 kg / 10 litres
Volume	1 m^3
Inflow and outflow areas	1 m^2
Darcy velocity	3.15×10^{-2} m/y

5.2 Modelling results

Two sets of simulations were performed using the Sugiyama and Fujita model, one that allowed quartz to precipitate and one in which quartz precipitation was disallowed. The decision to consider these two options was based on experience of running the model in order to attempt to achieve the best fit to the experimental data in Owada et al. (1999). *Figure 11* and *Figure 12* show the evolution of the CSH minerals and quartz in these two situations. Disallowing quartz precipitation significantly extends the 'lifetime' of the $Ca(OH)_2$ end member. This is due to elevated aqueous Si concentrations leading to lessened CSH dissolution in the case when quartz is not allowed to precipitate. When quartz precipitation is allowed, aqueous Si concentrations are held at quartz solubility (due to the equilibrium modelling assumptions) which drives CSH dissolution. It should be noted that quartz precipitation over the timescales modelled here is probably non-physical. However Owada et al. (1999) may allow quartz precipitation in their model because quartz is being used to represent a range of potential silica phases but this is not discussed in their paper.

Figure 13 to *Figure 16* show the evolution of pH and Ca^{2+} concentration in the Sugiyama and Fujita model, and the Owada et al. (1999) model and experiments. It is apparent from the pH curves (*Figure 13* and *Figure 14*) that the best fit to the data is achieved when quartz precipitation is disallowed in the model. Then, except for at very early times, the Sugiyama and Fujita model provides a much better fit to the pH data than the Berner-based model of Owada et al. (1999). The Sugiyama and Fujita model with quartz precipitation allowed follows a similar pH path to the Berner-based model.

In the Ca^{2+} concentration curves in *Figure 15* and *Figure 16* it can be seen that the Sugiyama and Fujita and Berner-based models give rise to quite different evolutions. The best fit to the Ca^{2+} data is probably provided by the Berner-based model, although the Sugiyama and Fujita models give a better fit at early times and seems to characterise the 'early peak' in the evolution better than the Berner models.

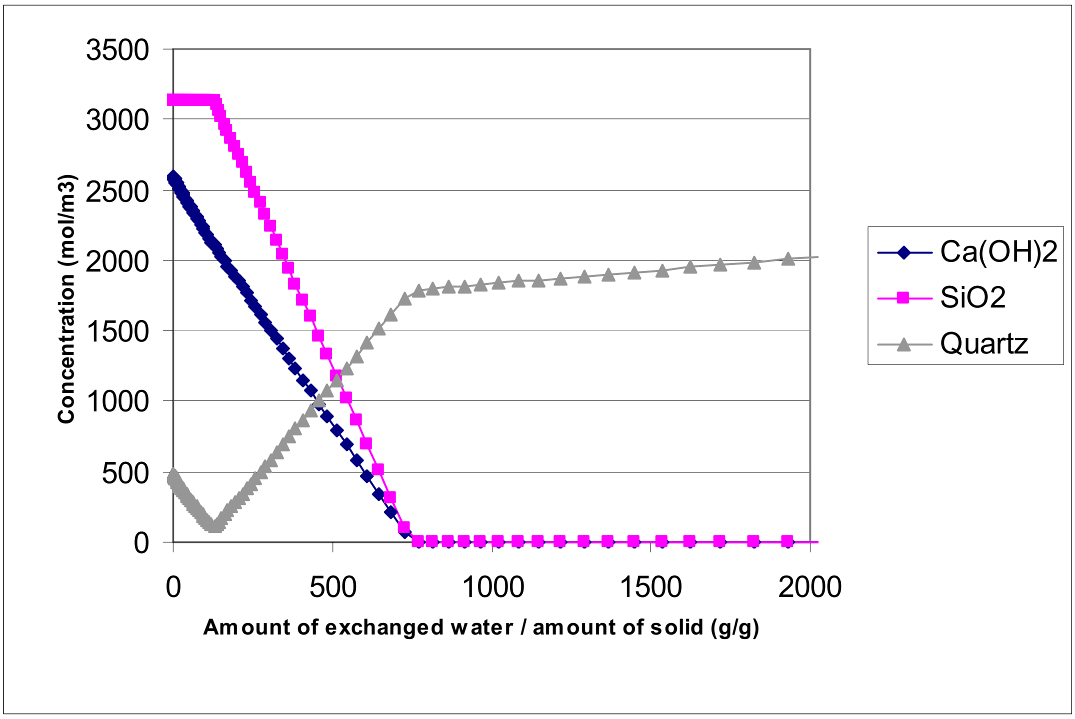

Figure 11: Evolution of CSH minerals and quartz in the Sugiyama and Fujita model allowing quartz precipitation as a function of amount of water exchanged.

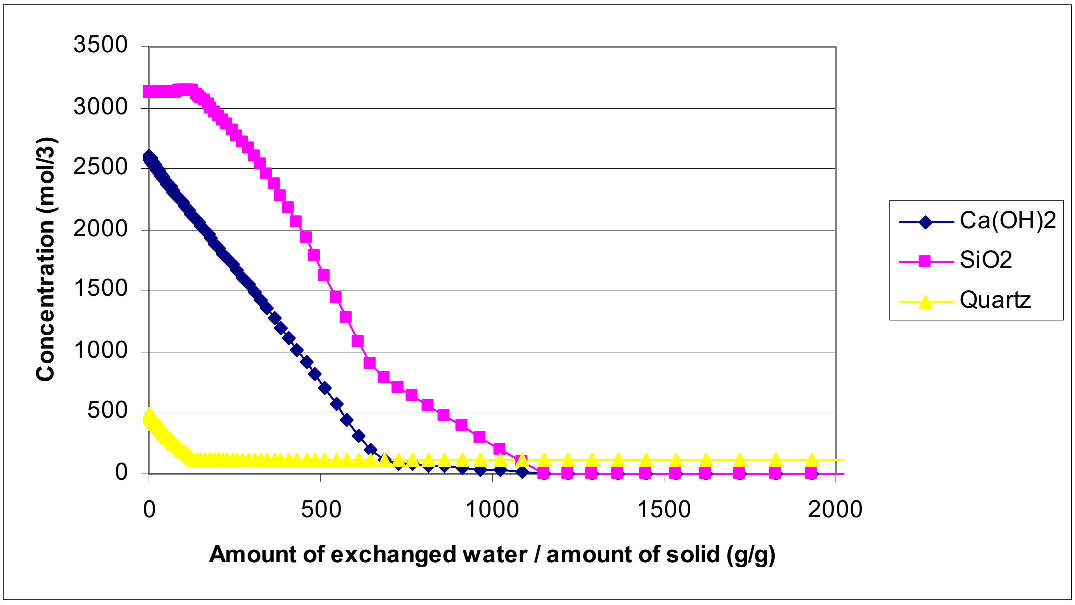

Figure 12: Evolution of CSH minerals and quartz in the Sugiyama and Fujita model disallowing quartz precipitation as a function of amount of water exchanged.

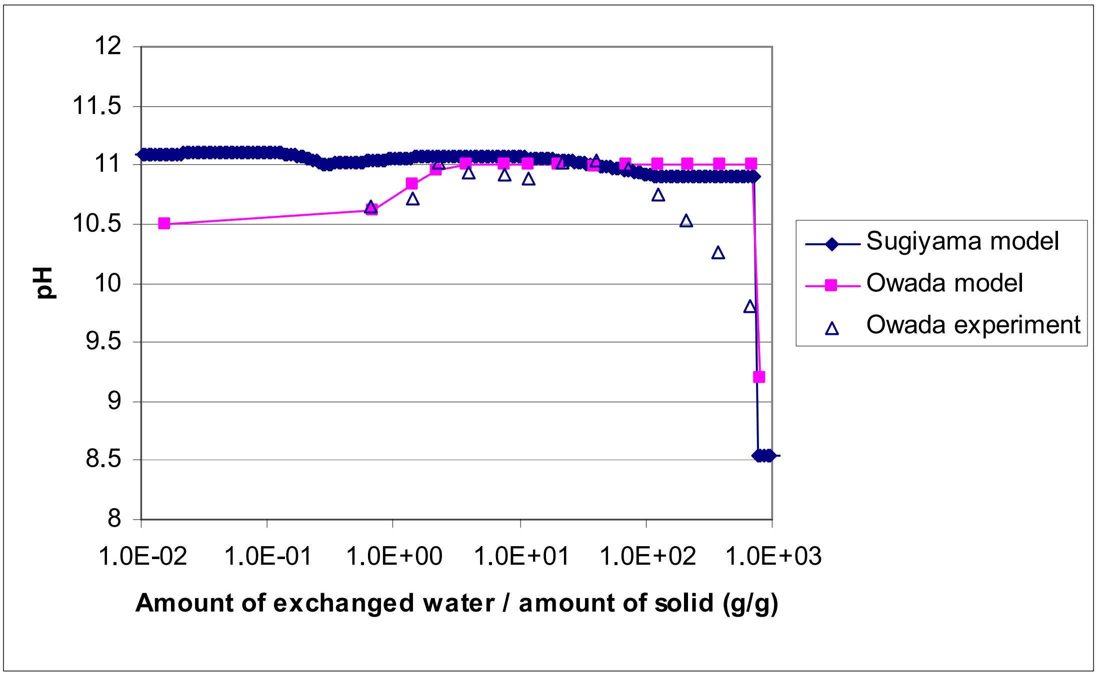

Figure 13: Evolution of pH as a function of amount of water exchanged. Sugiyama and Fujita curve from model allowing precipitation of quartz.

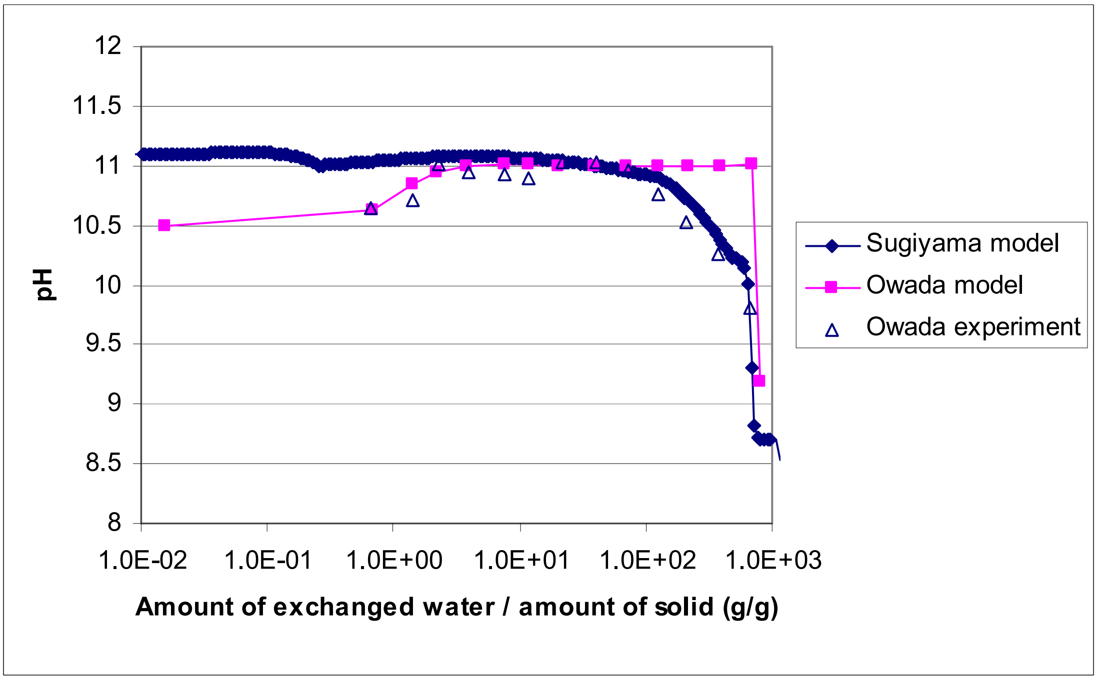

Figure 14: Evolution of pH as a function of amount of water exchanged. Sugiyama and Fujita curve from model disallowing precipitation of quartz.

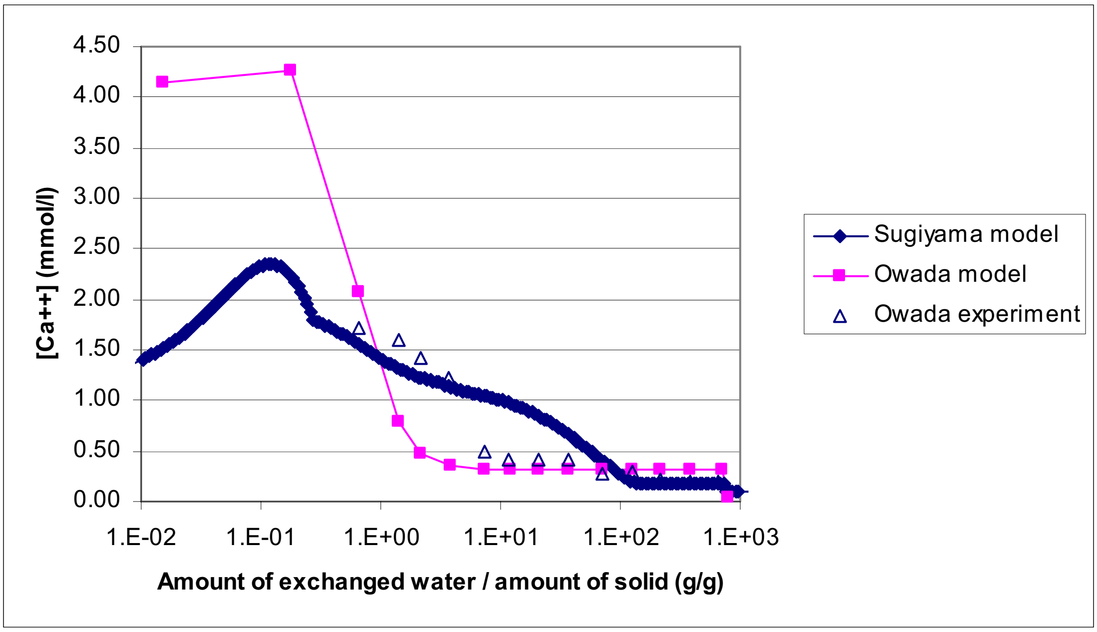

Figure 15: Evolution of Ca^{2+} *concentration as a function of amount of water exchanged. Sugiyama and Fujita curve from model allowing precipitation of quartz.*

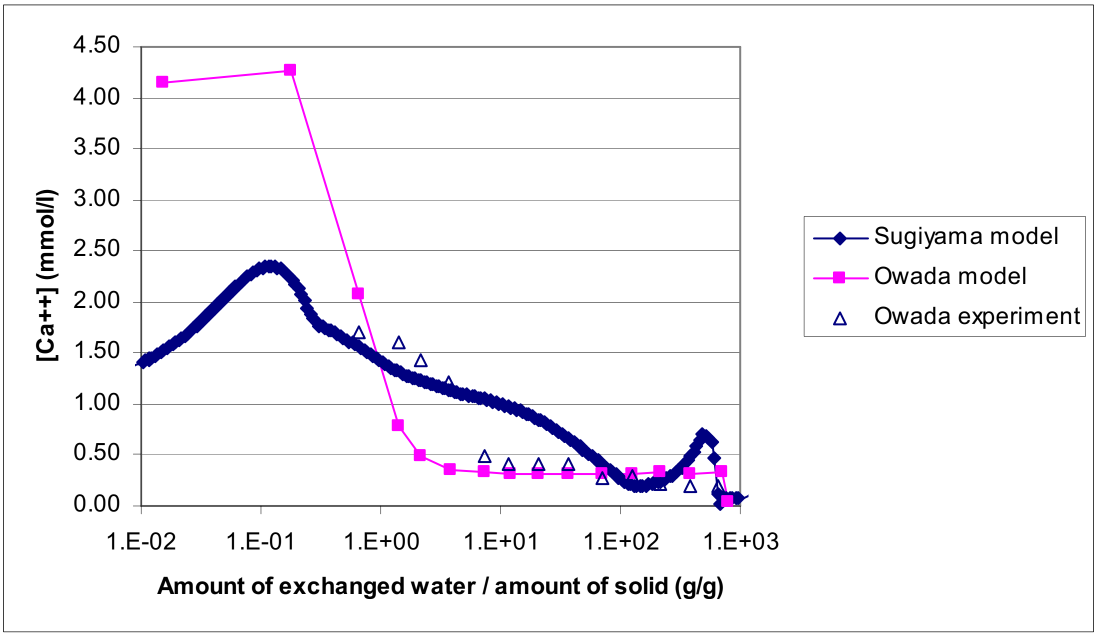

Figure 16: Evolution of Ca^{2+} *concentration as a function of amount of water exchanged. Sugiyama and Fujita curve from model disallowing precipitation of quartz.*

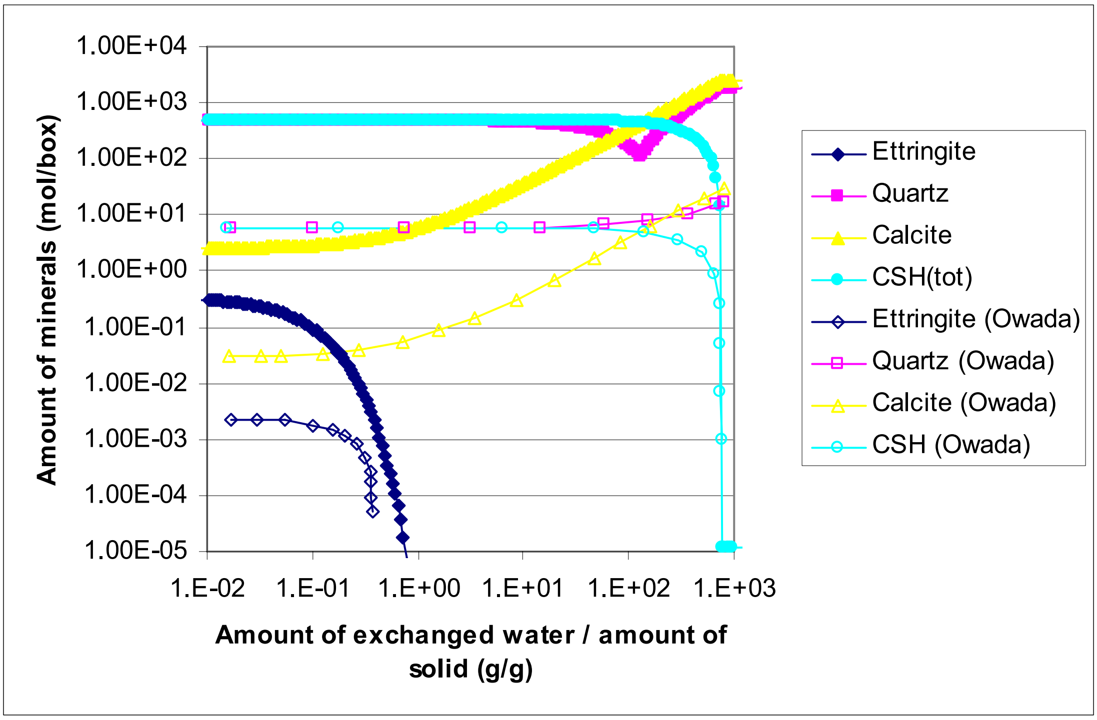

Figure 17: Evolution of the minerals in each model as a function of amount of water exchanged. Sugiyama and Fujita curves from model allowing precipitation of quartz.

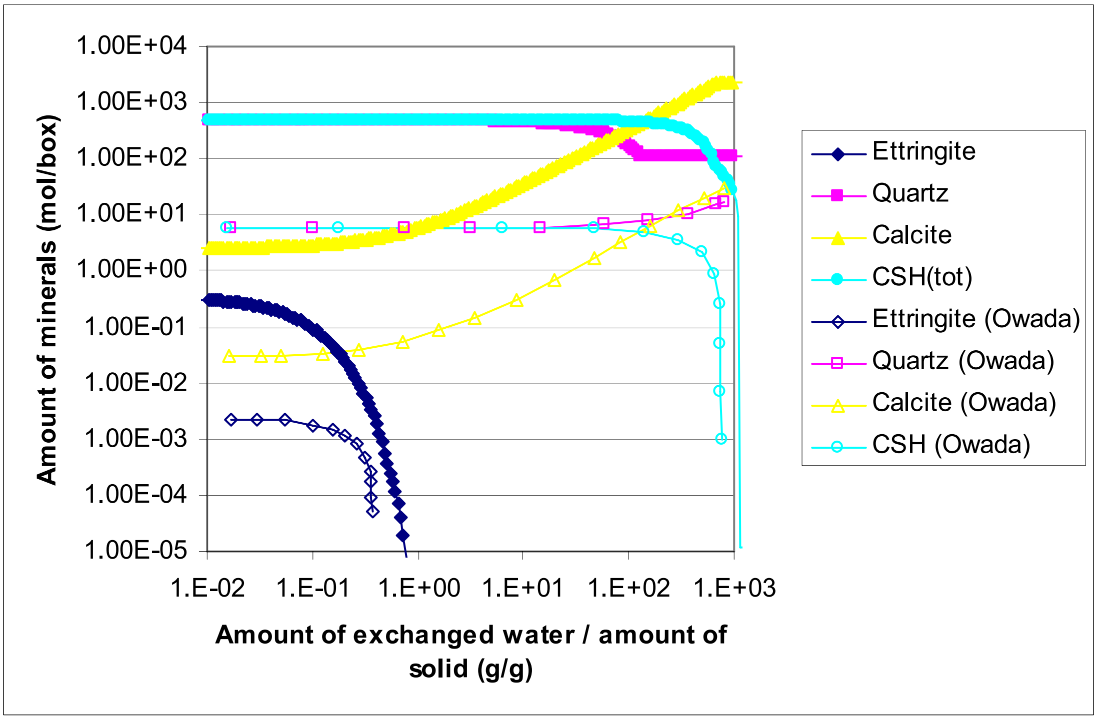

Figure 18: Evolution of the minerals in each model as a function of amount of water exchanged. Sugiyama and Fujita curves from model disallowing precipitation of quartz.

With quartz precipitation disallowed, the Sugiyama and Fujita model produces a ‘late peak’ in the Ca^{2+} evolution, which does not match the experimental data. It is possible that this feature of the evolution could be removed by allowing precipitation of an alternative silica species with a higher solubility (if an alternative silica species with a lower or equal solubility to quartz were used, the better fit to the pH data may be lost). All models predict similar evolution of ettringite and calcite (see *Figure 17* and *Figure 18*). Gibbsite was not observed in any of the models.

5.3 Summary

The Sugiyama and Fujita model matches the experimental data and modelling data of Owada et al. (1999) quite well, and would therefore seem to be a reasonable model of the interaction of low pH cement with groundwater. Its ability to fit the experimental data compares well with the Berner-based model presented by Owada et al. (1999).

The fit to the experimental data can be significantly improved by disallowing quartz precipitation in the model. This is at the expense of slightly poorer predicted Ca^{2+} concentrations, but it is possible that these might be improved by including an alternative secondary silica species in the model with a higher solubility than quartz, such as amorphous silica.

6 Conclusions

Low pH cements have reduced OPC contents due to blending with pozzolanic agents such as blast furnace slag, fly-ash, silica fume etc. SKB and Posiva have ruled out the use of blast furnace slag and fly-ash and are focusing on silica fume as a blending agent. To attain an entrained pore fluid with $pH \leq 11$, blending agents must comprise at least 50 wt % of dry materials. Because low pH cement has little, or no free portlandite, the cement consists predominantly of calcium silicate hydrate (CSH) gel with a Ca/Si ratio ≤ 0.8. Currently, SKB and Posiva have defined a pH limit ≤ 11 for cement grout leachates.

Although there are potential implications for the performance of the spent fuel and cladding due to the presence of hyperalkaline fluids from cement, the principal focus for safety assessment lies with the behaviour of bentonite. There are a number of potential constraints on the interaction of hyperalkaline cement pore fluids with bentonite, including mass balance, thermodynamic issues, mass transport, and kinetics, but none of these is likely to be limiting if conventional OPC cements are employed in repository construction. Nevertheless:

- Low-pH cements may supply approximately 50 % less hydroxyl ions than conventional OPC for a given volume of cement, but mass balance constraints are complicated by the uncertainty concerning the type of secondary minerals produced during cement-bentonite interaction.
- The change of aqueous speciation of silicon at pH 10 has a significant impact upon the solubility of montmorillonite and would thus constitute a rational choice of pH limit for cement-derived pore fluids, but it is unlikely that cement-based grouts could be developed to meet this limit.
- Control of mass transport by diffusion processes serves as a significant constraint over the amount of bentonite which can be degraded. Computer simulations indicate that porosity reduction is likely at the interface between cement and bentonite. However, it is not clear how the transport properties of bentonite may be modified due to mineral alteration processes.

- There are considerable uncertainties concerning the precise mechanism of the rate of montmorillonite dissolution at elevated pH. The rate of dissolution may be inhibited by the presence of dissolved Si (and perhaps Al), but this mechanism has yet to be confirmed at high pH. The type of secondary minerals assumed to form from cement-bentonite interaction will also have a significant impact upon the rate of montmorillonite dissolution.

Low-pH cement systems have received little attention thus far regarding the development of models for the chemical evolution of pore fluids. Low Ca/Si CSH gels show preferential leaching of Si, which is in marked contrast with gels of greater Ca/Si ratio. Models apparently capable of predicting pore fluid composition coexisting with low Ca/Si CSH gels are those of Berner (as modified by Harris et al., 2002) and that of Sugiyama and Fujita (2005).

The solubility of silica in pore fluids coexisting with low Ca/Si gels may exceed that of amorphous silica, and may pose problems regarding the stability of montmorillonite in relation to framework silicates such as feldspars.

It is necessary to use additives such as superplasticiser to improve the workability of low-pH cements. These organic additives have the potential to complex with radionuclides and enhance their mobility. Data regarding these properties are sparse and require further investigation.

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