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The long-term stability of cement

– Leaching tests

Ingemar Engkvist, Yngve Albinsson,
Wanda Johansson Engkvist

Chalmers University of Technology,
Göteborg, Sweden

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ABSTRACT

The concrete construction in the Swedish repository for long-lived low and intermediate level waste (SFL 3-5) will give a stable chemical nearfield environment for 10^5 years. The pH is expected to exceed 12 for the life time for most of the radionuclides in the repository in both saline and non-saline groundwaters.

This is shown by static leaching experiments performed in saline and non-saline granitic groundwater conditions. Five gram portions of crushed Ordinary Portland cement paste were equilibrated with 20 ml of synthetic saline or non-saline groundwater in a nitrogen atmosphere. Each week 12 ml (60%) of the water was replaced. The withdrawn water was used for chemical analyses and the results were used to monitor the degradation of the cement paste.

After eighty weeks, some samples were analysed for mineral composition and compared with the original unleached paste. The results indicated no secondary ettringite or calcite formation. The results also supported the conclusion that the salinity of the contacting water is of minor importance for the long-term performance of the cement paste.

SAMMANFATTNING

Betongkonstruktionerna i det svenska förvaret av låg och medelaktivt avfall (SFL 3-5) ger en stabil kemisk miljö i närområdet i hundratusentals år. pH förväntas överstiga 12 under livstiden för de flesta av radionukliderna i förvaret och gäller både för söta och salta grundvattenförhållanden.

Detta har visats med statiska lakningsfösök i salta resp. söta vattenförhållanden. Portioner av fem gram krossad Standard Portland cementpasta jämviktades med 20 ml salt eller sött syntetiskt granitiskt grundvatten i kvävgasatmosfär. Varje vecka utbyttes 12 ml (60%) av vattnet. Det utbytta vattnet analyserades och resultatet användes för att indikera nedbrytningen av cementpastan.

Efter åttio veckor gjordes analyser av några prover för mineralogisk bestämning. Resultaten visar vid jämförelse med olakad cementpasta att ingen sekundär ettringit eller kalcit hade bildats. Resultaten stöder också slutsatsen att salthalten i grundvattnet är av ringa betydelse för cementpastans funktion att ge en stabil kemisk miljö.

SUMMARY AND CONCLUSIONS

In order to predict the long-time stability of cement in granitic groundwaters, leaching tests were performed. Six 5 g portions of crushed cement paste were each equilibrated with 20 ml of saline or non-saline synthetic ground water in polypropylene test tubes. The tubes were gently agitated by rotating them slowly. Sixty percent of the water volume was exchanged weekly. The tubes were stored and the water changes were performed in a nitrogen filled glovebox at ambient temperature (18-25°C).

The leach water was analysed for sodium, potassium, calcium, hydroxide, chloride, sulphate, silica and aluminium. These analyses give not only an indication of the degradation process of the cement but also indicate the the time dependence of the chemical conditions in the near-field of a concrete based repository.

After eighty weeks of leaching, samples were analysed for mineral composition and compared with non-leached samples.

The most important conclusion from a safety assessment point of view is that a concrete construction gives a stable alkaline chemical environment for more than 10^5 years in a deep underground repository where the hydraulic gradients are small and the groundwater flow is slow. There is no point in considering a scenario where the cement has been leached to the degree where pH drops below approximately 12.5 and this is true both for non-saline and saline groundwater conditions.

Ettringite formation that causes expansion by binding large amounts of water (Lea, 1970) has not been observed in these experiments. However, the formation of ettringite could not be ruled out at higher sulphate concentrations (*e.g.* in sulphate rich bentonite porewaters or sulphate from degradation of cation exchange resins).

There is no evidence for excessive carbonation of the cement in the experiments. The calcite originates from setting and the storage of the cement and not from the leaching experiments.

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1 INTRODUCTION

Concrete or cement paste is often considered to be used as a technical barrier in a repository for radioactive waste. Cement can also be used as a solidification material for a vast variety of wastes. Due to the leaching of alkalies present in fresh cement, the cement will initially induce a highly alkaline water with a hydroxide concentration of 0.3-0.4 mole·l^{-1} which corresponds to a pH about 13-13.5. However, this leaching process is fast and after all the alkalis have been leached and transported away, the hydroxide concentration drops to approximately 0.03-0.04 mole·l^{-1} (pH $\approx$ 12-12.5) determined by the solubility of portlandite ($Ca(OH)_2$) (Baes, 1976).

In order to predict the chemical behaviour of the radioelements, such as speciation, solubility and sorption, it is essential to be able to evaluate the long-term chemical stability of a cementious environment. It is therefore important to study the time scale for which portlandite is the key mineral determining the water chemistry. Investigations of pore water evolution has been studied experimentally and/or by modelling by several authors; Berner (Berner, 1992), Greenberg and Chang (Greenberg, 1965), Glasser *et. al.* (Glasser, 1985:1),(Glasser, 1985:2), Atkins *et. al.* (Atkins, 1991), Lachowski *et al.* (Lachowski, 1980), Neall (Neall, 1996), Kondo et al (Kondo, 1981), Savage and Rochelle (Savage, 1993) *etc.* However, most of the investigations deal with the distilled water and cement interaction and only a few with groundwater and cement.

Since both saline and non-saline groundwater can be expected in a Swedish repository for long-lived intermediate level waste (SR95, 1995), leaching tests of Ordinary Portland Cement, OPC, is performed with both types of waters.

2 CEMENT

2.1 CEMENT CHEMISTRY NOMENCLATURE

In some cases, cement nomenclature will be used for practical reasons. In other cases, chemical formulae are used for clarification. The following abbreviations are common for cement chemistry (Lea, 1970):

C	CaO	K	K_2O
S	SiO_2	N	Na_2O
A	Al_2O_3	M	MgO
F	Fe_2O_3	H	H_2O
$\bar{S}$	SO_3		

2.2 CEMENT CHEMISTRY

Portland cement is processed by thermal treatment of a finely ground mixture consisting mainly of lime stone, sand and clay. The main components of the mixture are compounds containing calcium, aluminate, silicate and iron. The ranges of the elementary analysis of Swedish Portland cement, expressed in terms of oxides, are given in Table 2-1.

Table 2-1. Chemical composition of Swedish Portland cement (Trädgårdh, 1996)

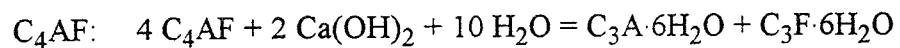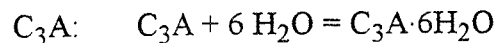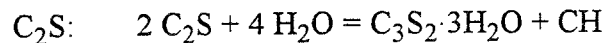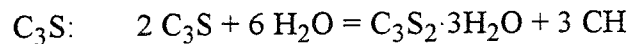| Oxide	Notation	Weight %
CaO	C	63
SiO_2	S	20
Al_2O_3	A	4.3
Fe_2O_3	F	2.2
MgO	M	1.5 - 3.8
SO_3	$\bar{S}$	1.6 - 3.3
K_2O	K	0.1 - 1.5
Na_2O	N	0.0 - 0.5

These compounds are combined in the clinker (the final product from the thermal treatment) after burning, and the compounds C_2S, C_3S, C_3A and a ferrite, often close to C_4AF in composition, are formed (Lea, 1970). An average phase composition of the OPC used in the experiments is in Table 2-2.

Table 2-2. Average content of major phases in OPC (Slite cement)

(Trädgårdh,1996).

Component	Notation	Chemical formula	Content, % by weight
Tricalcium silicate	C_3S	$(CaO)_3SiO_2$	58
Dicalcium silicate	C_2S	$(CaO)_2SiO_2$	13
Tricalcium aluminate	C_3A	$(CaO)_3Al_2O_3$	8
Tetracalcium aluminate ferrite	C_4AF	$(CaO)_4Al_2O_3Fe_2O_3$	7

The hydration products of the main solid phases in Portland cement are (Czernin, 1969):

C_3S: $2\,C_3S + 6\,H_2O = C_3S_2 \cdot 3H_2O + 3\,CH$

C_2S: $2\,C_2S + 4\,H_2O = C_3S_2 \cdot 3H_2O + CH$

C_3A: $C_3A + 6\,H_2O = C_3A \cdot 6H_2O$

C_4AF: $4\,C_4AF + 2\,Ca(OH)_2 + 10\,H_2O = C_3A \cdot 6H_2O + C_3F \cdot 6H_2O$

Thus a considerable amount of calcium hydroxide is present in the hydrated cement. Also calcium silicate, calcium aluminate and calcium ferrite phases are formed.

When the cement is hydrated, a matrix with some crystalline components and a calcium silicate hydrate is formed. In the solid there is an initially water filled pore system, constituting ca 10 - 15 % of the volume. The cement crystallises slowly, and gel phases are found after a very long time (Lea, 1970).

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3   EXPERIMENTAL

Six 5 g portions of crushed cement paste were each equilibrated with 20 ml of saline or non-saline synthetic ground water in polypropylene test tubes. The tubes were gently agitated by rotating them slowly. Sixty percent of the water volume was exchanged weekly. The tubes were stored and the water changes were performed in a nitrogen filled glovebox at ambient temperature (18-25°C).

The cement could technically be considered fully hydrated since it was set in 1982 and then stored in water. The cement paste was crushed in a mortar and a grain size of 0.063 to 0.125 mm was collected. This operation was performed in a nitrogen filled glovebox to avoid further carbonation.

3.1   WATER

The composition of the synthetic non-saline and saline groundwater is in Table 3. The saline water was composed by NAGRA, Switzerland and SKB, Sweden and has the abbreviation NASK (Lagerblad, 1995). The non-saline groundwater was Allard water, (Lagerblad, 1995), and both waters represent granitic conditions. The waters were prepared in room atmosphere but were later transferred into the glove box containing nitrogen. Table 3-1 shows the composition of the waters.

3.2   WATER CHANGES

Each week the slow agitation was stopped and the test tubes were taken out of the glovebox and centrifuged for one hour with an average centrifugal field of 10 000g. Immediately afterwards the tubes were transferred back into the box and 12 ml of the supernatant was exchanged with unreacted groundwater. The withdrawn water was stored in nitrogen atmosphere for future chemical analysis.

Table 3-1   Composition of the synthetic granitic groundwaters used in the experiments

	Non-saline[1]		Saline[2]	
	mg/l	mmole/l	mg/l	mmole/l
Na	65[3]	2.8	3320	144[3]
K	3.9	0.1	80	2.0
Ca	18	0.5	800	20
Mg	4.3	0.2	10	0.4
Cl	70	2.0	6390	180
HCO_3	123	2.0	120	2.0
SO_4	9.6	0.1	380	4
H_4SiO_4	21	0.2		
pH	8.0-8.2		7.7	

[1] Allard water

[2] NASK water

[3] Sodium concentration is slightly variable due to titration to desired pH.

3.3   WATER ANALYSES

The leach water samples were centrifuged for 30 min. with an average field of 17 000 g. For the anion analyses, 0.1 ml of the saline samples was transferred into new polypropylene test tubes and 9.9 ml of Milli-Q water was added to each sample. In the case of the non-saline samples, 1.0 ml was diluted with 9.0 ml of water. For cation analyses the samples were diluted in the same way but with 0.1 mole·l^{-1} HCl. The cations Na, K and Ca were analysed with ion chromatography, IC, (DX-100, Dionex, USA) with a CS12 column (Dionex, USA). The anions Cl and SO_4 were also analysed with IC, but with a AS4A-SC column (Dionex, USA). Silica and aluminium concentrations were analysed by spectrophotometer (Carlberg, 1972) and SS 028210 (Swedish Standard). The hydroxyl ion concentration was determined by titrations using a ABU 91 automatic titrator (Radiometer, Denmark). In samples where the ionic strength was too low for accurate responses from the electrodes, 1 ml of 2 mole·l^{-1} NaCl was added The methods for water analyses and their detection limits are summarised in Table 3-2.

Table 3-2   Summary of methods used for chemical analysis and their corresponding detection limits.

Element/ion	Method	Detection limit
Na	Ion chromatography	1 ppm
K	Ion chromatography	0.5 ppm
Ca	Ion chromatography	5 ppm
Mg	Ion chromatography	0.5 ppm
Si	Spectrophotometry	1 ppm
Al	Spectrophotometry	5 ppb
SO_4	Ion chromatography	5 ppm
Cl	Ion chromatography	1 ppm
OH	Titration	1 mmole·l^{-1}

3.4   SOLID PHASE ANALYSIS

The cement paste analysis was performed by the British Geological Survey, Nottingham, England and Department of Geology, University of Manchester, Manchester, England. The techniques used are in Table 4. Three samples were used for the analyses; unleached, leached 80 steps with saline groundwater and leached 80 steps with non-saline groundwater. The unleached sample was from the original material (crushed) and had been stored dry in the glovebox.

Table 3-3 Summary of methods for solid phase analysis

Method	Abbreviation
Scanning electron microscopy	SEM
X-ray diffraction analysis	XRD
Termogravimetric analysis	TGA
Analytical transmission electron microscopy	ATEM
Energy-dispersive X-ray microanalysis	EDXA

4 RESULTS

From a safety assessment point of view, the most important parameter to study in these kinds of leaching tests is the hydroxyl ion concentration in the cement pore water. Since pH measurements in these kinds of waters with a pH exceeding 12 are very problematic (Baes, 1976), we simply chose to present the total (complexed and uncomplexed) hydroxyl ion concentration. The results are in Figure 1. For illustrative reasons, results of the ion analyses are related to an "apparent pH" which is calculated from titration data by taking into account complexed hydroxide and are plotted as a solid line in all graphs. The stability constant for $CaOH^+$ was taken from "Hydrolysis of Cations" (Baes, 1976) and corrected by extrapolation for ionic strength.

The initial high hydroxyl ion concentration that lasted for a few leaching steps was the result of leaching and dilution of NaOH and KOH. It was followed by the dissolution of portlandite giving an equilibrium hydroxyl ion concentration of 0.04 mole·l⁻¹ (corresponding to pH 12.5). By leaching step 50 the concentration started to decrease which can be interpreted as the result of the complete removal of portlandite $(Ca(OH)_{2,s})$. This leaching pattern has been observed by others e.g. (Atkinson, 1985).

The results of the ion analyses are discussed in the following sections. The graphs shown are direct representations of the concentrations together with graphs for the massbalance (total dissolved amount) of the system, calculated by:

$$C_{1,\text{before reaction}} = C^0 \tag{1}$$

$$C_{1,\text{ after reaction}} = C_{1,\text{analysis}} \tag{2}$$

$$C_{2,\text{before reaction}} = (8C_{1,\text{before reaction}} + 12C^0)/20 \tag{3}$$

$$C_{2,\text{ after reaction}} = C_{2,\text{analysis}} \tag{4}$$

$$\text{Total dissolved amount [moles]} = (C_{\text{after reaction}} - C_{\text{before reaction}}) \cdot 0.012 \tag{5}$$

It should be noted that a negative sign for total dissolved amounts merely indicates no dissolution but precipitation, c.f. SO_4, Si and Cl (not measured in the saline water experiment).

4.1   WATER CHEMISTRY

In all water analyses, magnesium was detected for but was never found in the leach solutions. This is not unexpected due to the low solubility of brucite $(Mg(OH)_{2,s})$ at these high pH-values (Baes, 1976).
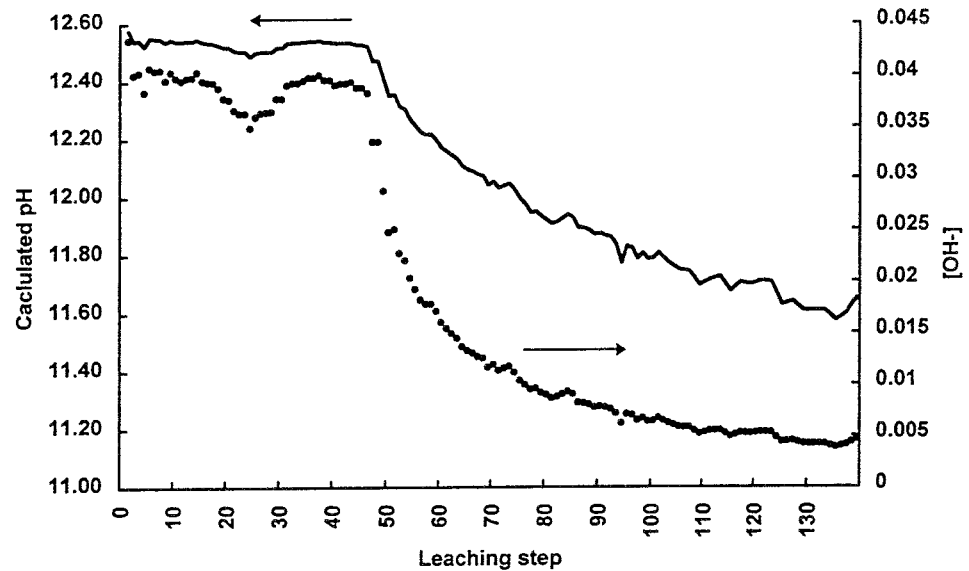

Figure 4-1. Results of titrations of the non-saline leachwaters.

4.1.1   Non-saline groundwater leached sample

Hydroxide
The development of hydroxyl ion concentrations throughout the experiment is shown in Fig 4-1 above. These results were used for calculating the pH in the solutions. The calculations are described in Sect. 4.

Sodium and potassium
The leach pattern for sodium and potassium is typical for a OPC cement (Glasser, 1985:1) where both element concentrations reach as high value as several $mmole \cdot l^{-1}$. The sodium and potassium concentrations very quickly decrease to the concentrations of the unreacted groundwaters *c.f.* Figs. 4-2, 4-3, 4-4, and 4-5. When the portlandite has dissolved sodium is leached from the cement. This pattern could be explained by either dissolution of a sodium containing CSH phase or that new surfaces containing sodium hydroxide are being exposed to water. The latter is however, contradicted by the determinations of the hydroxide concentration.

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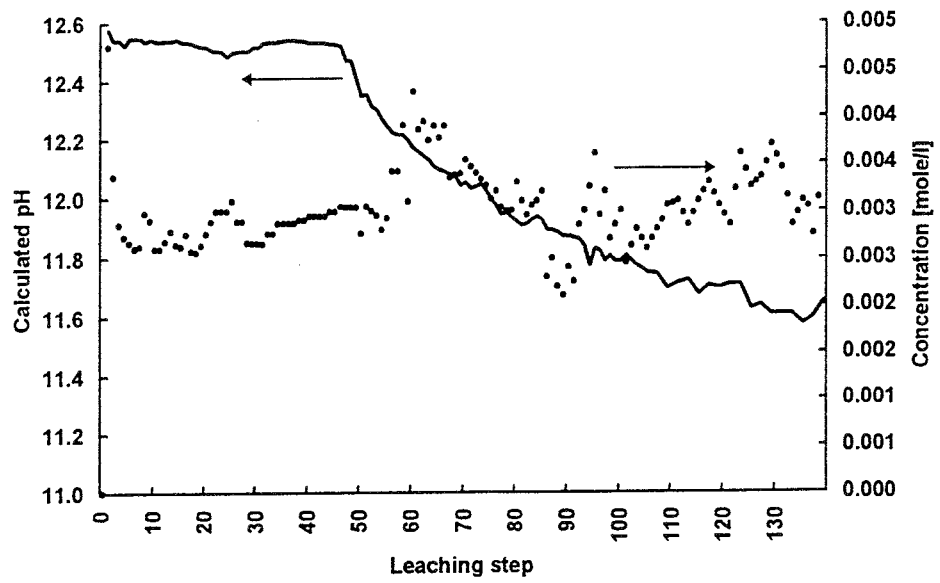
Figure 4-2. Concentration of sodium in non-saline groundwater leachate.

Figure 4-3. Total amount dissolved sodium from non-saline groundwater leached cement paste

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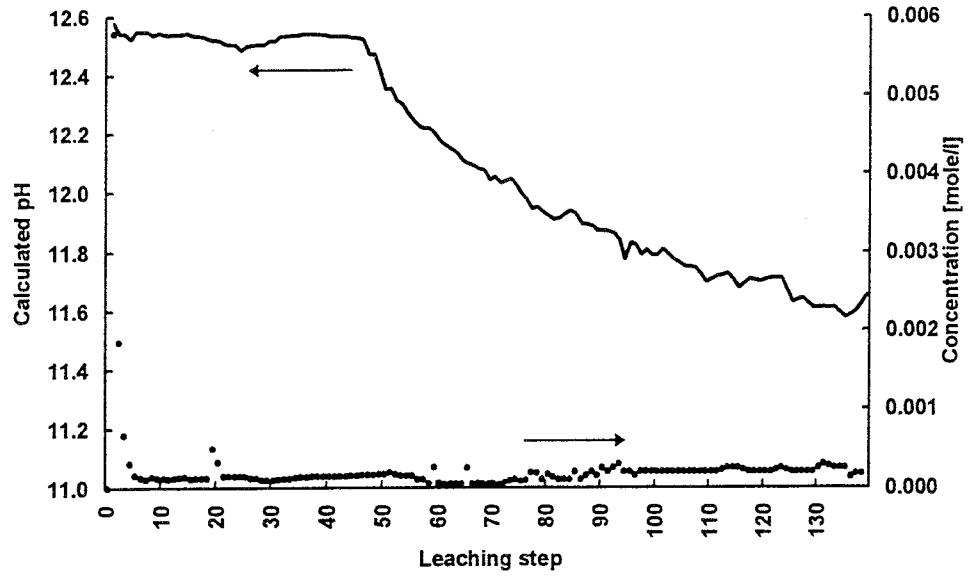
Figure 4-4. Concentration of potassium in non-saline groundwater leachate.

Figure 4-5. Total amount dissolved potassium from non-saline groundwater leached cement paste

10
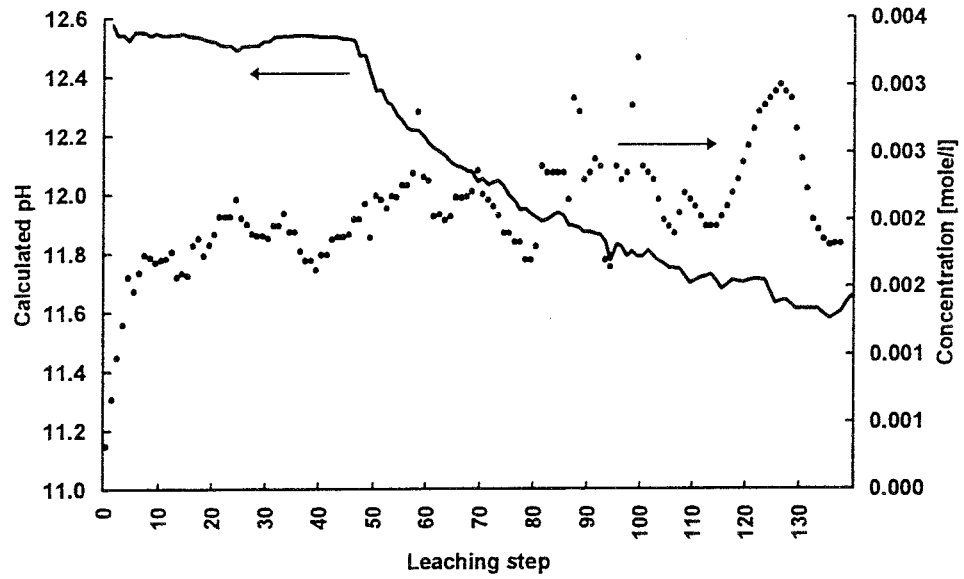
Figure 4-6. Concentration of chloride in non-saline groundwater leachate.

Chloride

Chloride is being precipitated from the groundwater but at such small amounts that it is really not significant. Furthermore, solid phase analyses did not identify any chloride containing phases. After about fifty leaching steps, chloride is beginning to dissolve. At leching step 100, the paste has released the previously precipitated chloride and the material is beginning to be depleted from initial chloride, c.f. Figs 4-6 and 4-7.
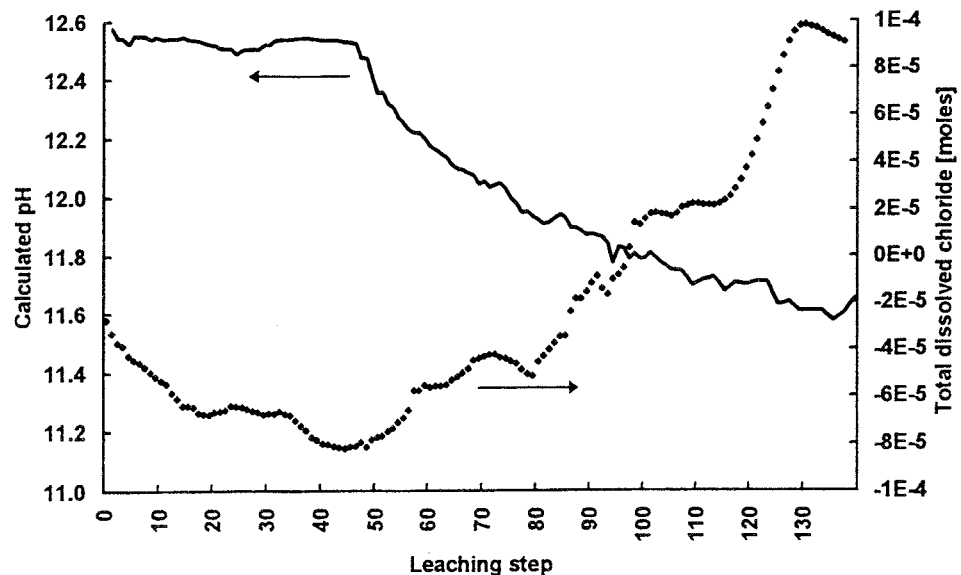
Figure 4-7. Total amount dissolved chloride from non-saline groundwater leached cement paste

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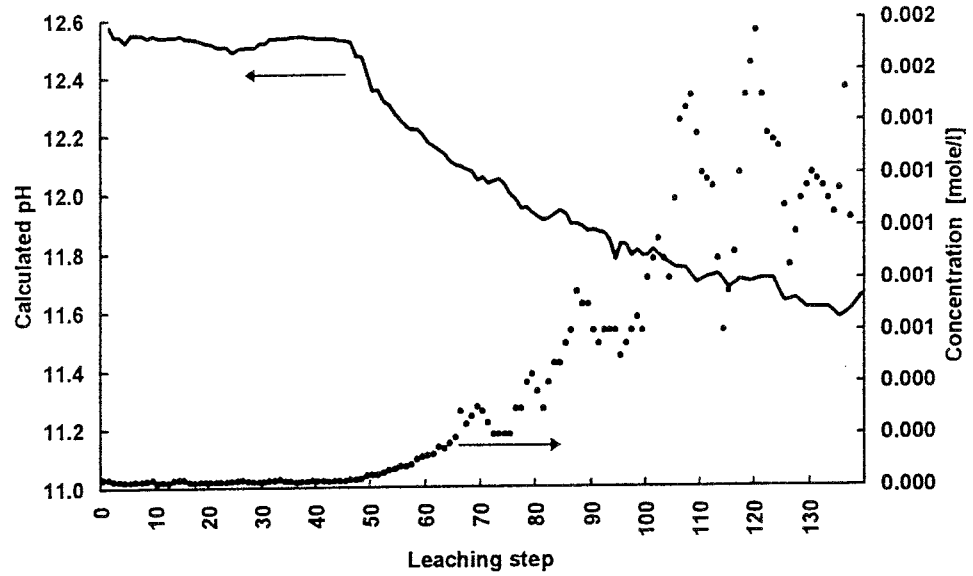
Figure 4-8. Concentration of sulphate in non-saline groundwater leachate.

Sulphate

The possibility of forming ettringite or thaumasite is interesting in a performance assessment point of view. The experiment shows small amounts of sulphate being precipitated but only less than 50 μmoles with a maximum at leaching step around sixty. The pattern afterwards is clearly a dissolution of sulphate. Solid phase analyses indicated presence of ettingite and thaumasite, but in minor amounts.
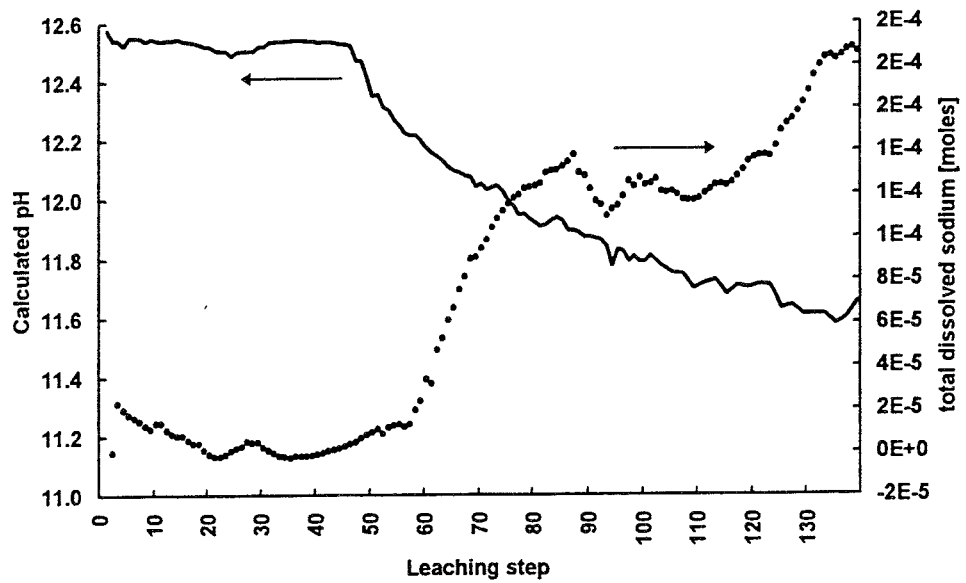

Figure 4-9. Total amount dissolved sulphate from non-saline groundwater leached cement paste.
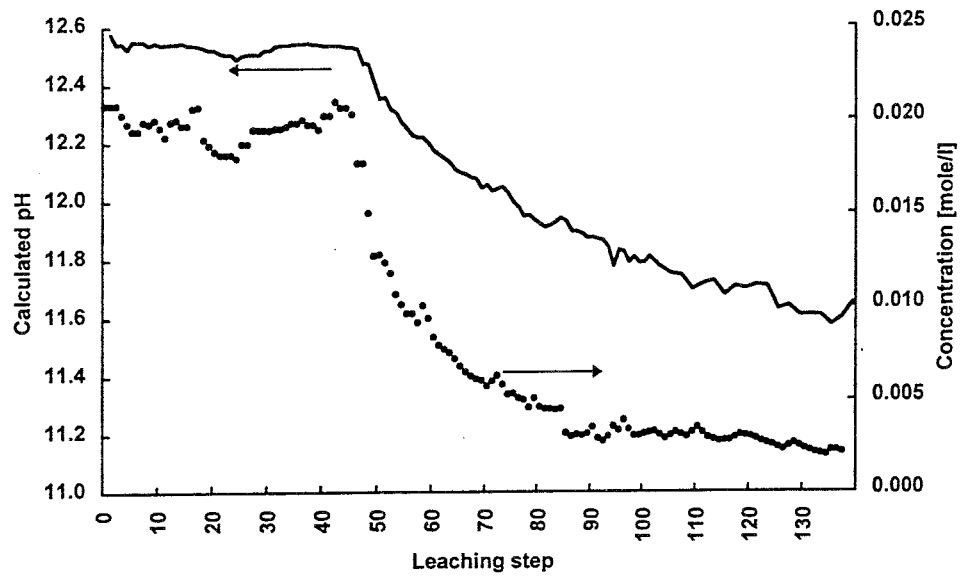
Figure 4-10. Concentration of calcium in non-saline groundwater leachate.

Calcium

The leaching pattern of calcium is typical for cement paste (Glasser, 1985:1). At steps 40-50 the concentration decreases dramatically which can be interpreted as the complete dissolution of portlandite *c.f.* Fig. 4-10 This transition from congruent to incongruent dissolution can be observed in Fig 4-11 where the first part of the experimental values lies as a straight line but after leaching steps 40-50, as a curve.

Figure 4-11. Total amount dissolved calcium from non-saline groundwater leached cement paste

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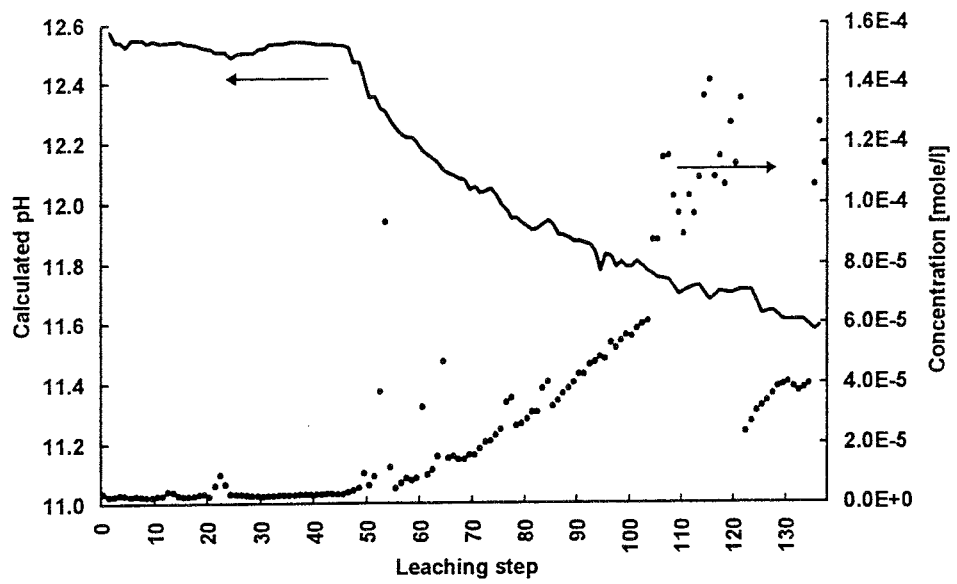
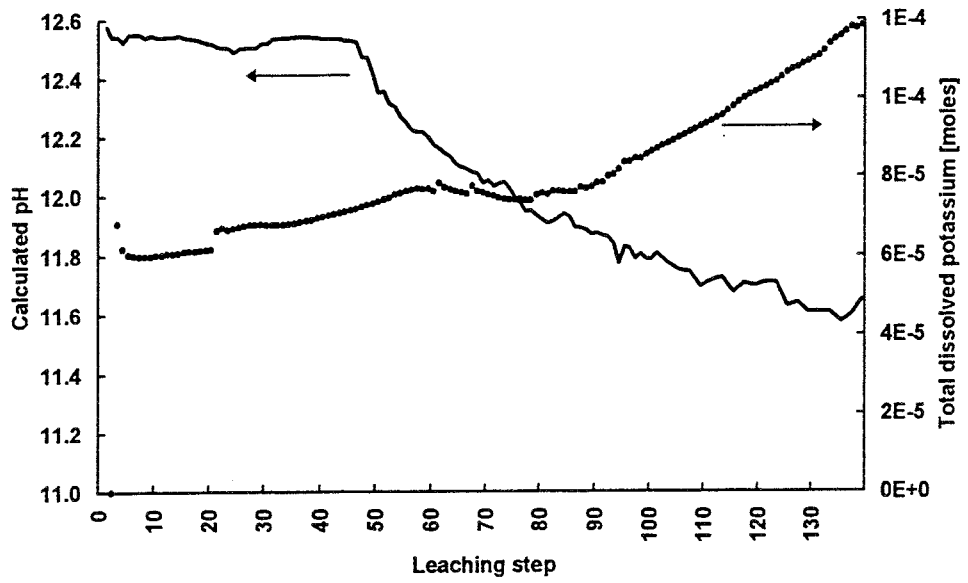*Figure 4-12.* Concentration of silica in non-saline groundwater leachate.

Silica

Although the concentration of silica in the leach water is increasing from about fifty in the experiment, it is less than in the unreacted groundwater, indicating a continuous precipitation. As can be seen from the plot of concentration vs. leaching step, the analyses show large errors at the end of the experiment which could be due to a colloidal fraction being formed c.f. Figs. 4-12, 4-13). It is not possible to separate this fraction from the water phase.
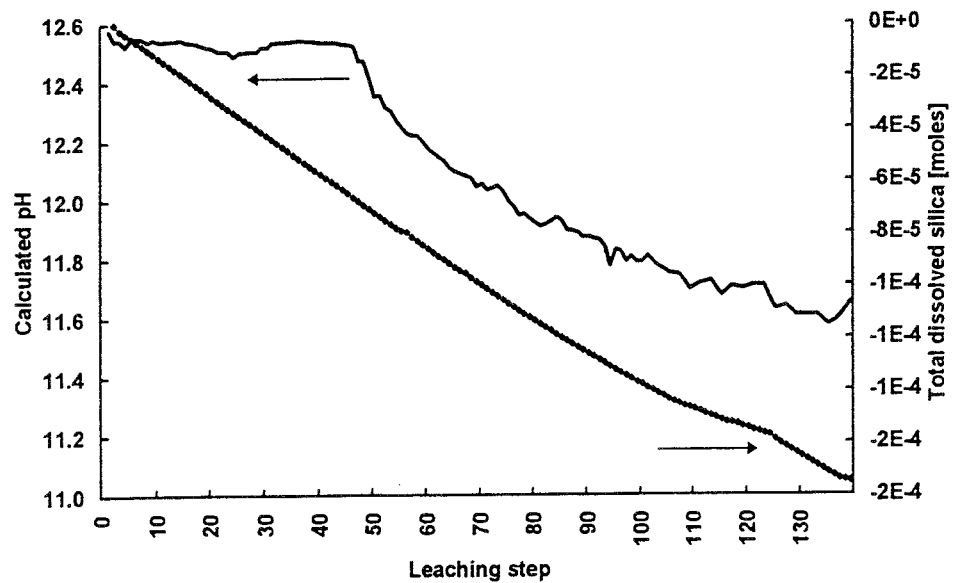
Figure 4-13. Total amount dissolved silica from non-saline groundwater leached cement paste

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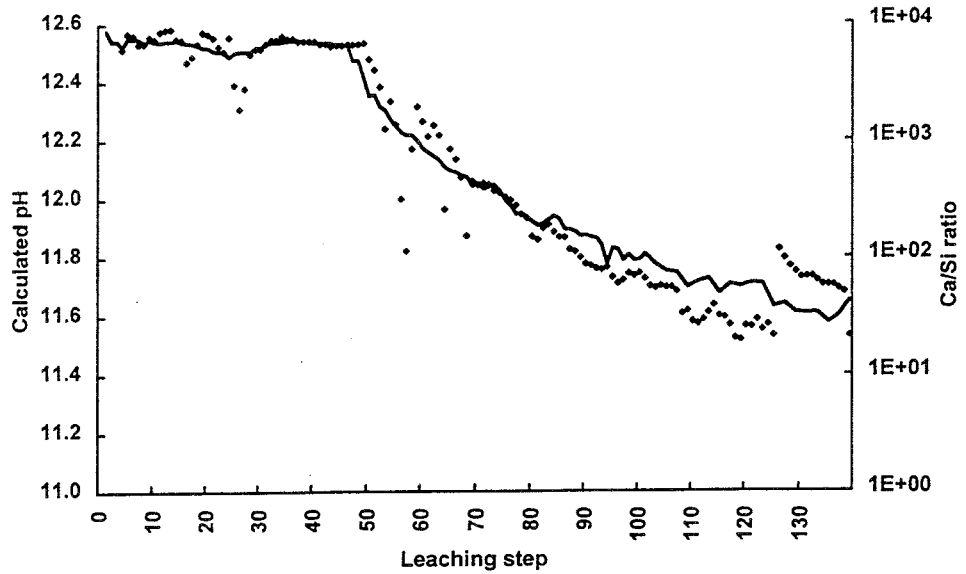
Figure 4-14. *Ratio of the concentration ratio calcium to silica as a function of leaching steps. Dots inidate Ca/Si-ratio.*

Ca/Si ratio

The ratio between Ca and Si superimpose the pH curve in Fig 4-14. This is a coincidence due to the choice of the secondary y-axes. However, the pattern again shows the incongruent dissolution of the CSH phase where Ca is continuously leached and Si is being enriched in the phase, *c.f.* Figs 4-10, 4-11, 41-12, and 4-13.
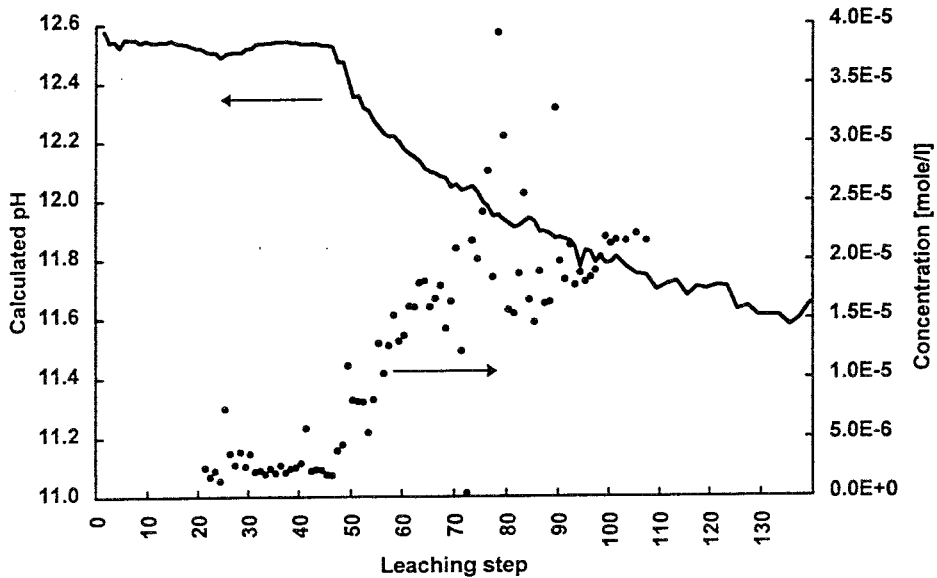
Figure 4-15. *Concentration of aluminium in non-saline groundwater leachate.*

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Aluminium

Since aluminium was not analysed from the start of the experiment, massbalance is not possible to calculate. However, from Fig. 4-15 an increase of aluminium concentration as a function of leaching steps can be observed. The concentrations are very low and in the range of $\mu mole \cdot l^{-1}$

4.1.2 Saline groundwater leached sample

Hydroxide

The development of hydroxyl ion concentrations throughout the experiment is shown in Fig 4-16 below. These results were used for calculating the pH in the solutions. The calculations are described in Sect. 4.

Sodium and potassium

The water analyses of the leach water from the saline leached samples show the same pattern for potassium as the non-saline leached samples *c.f.* Figs 4-17 and 4-18. The sodium concentration is too high in the saline groundwater and no real leaching pattern is observed. It is however clear that sodium is being enriched in the solid during the first phase of the experiment but later continuously leached out, *c.f.* Figs. 4-19, 4-20. As the main constants in the saline groundwater are sodium and chloride, no analysis was made for chloride.
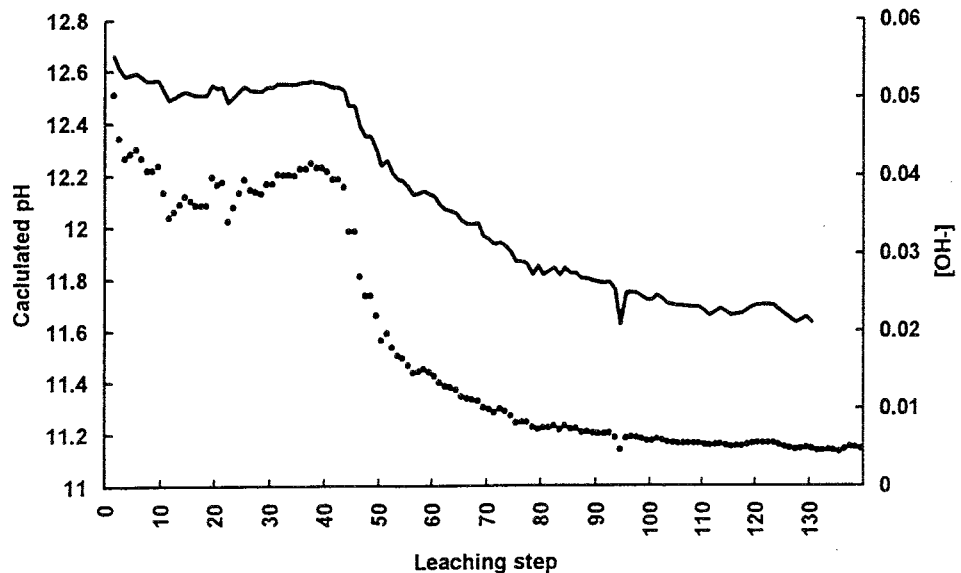
Figure 4-16. Concentration of aluminium in non-saline groundwater leachate.

16

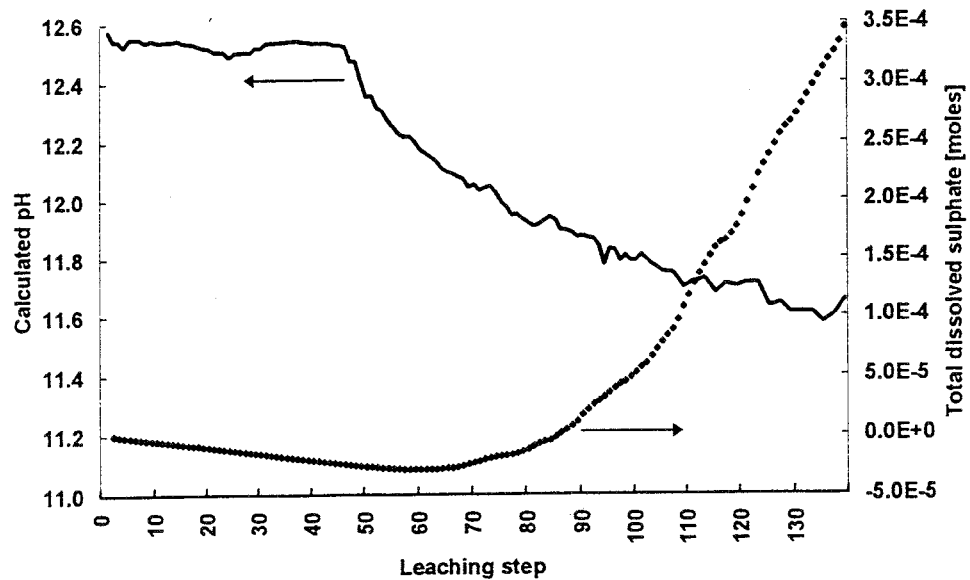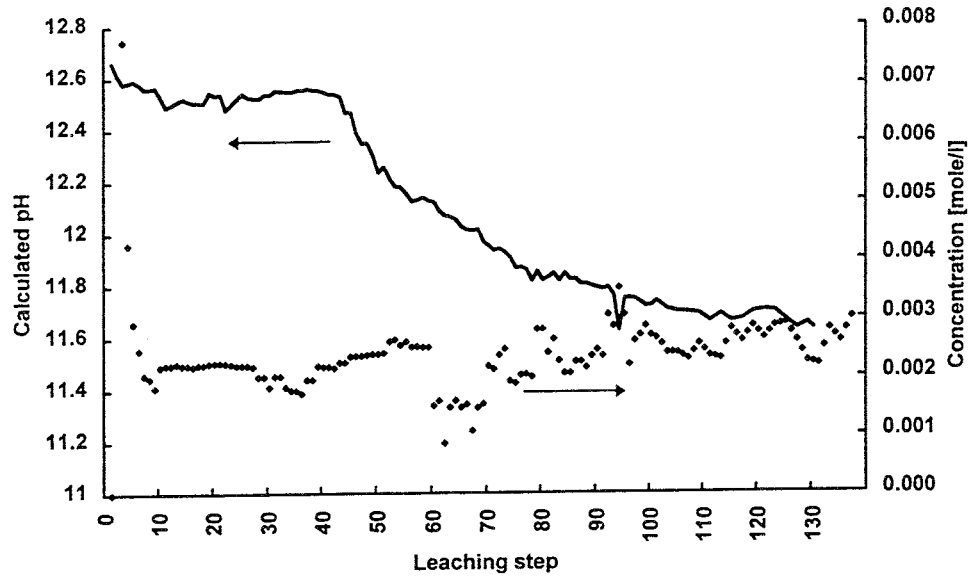*Figure 4-17.* Concentration of potassium in saline groundwater leachate.
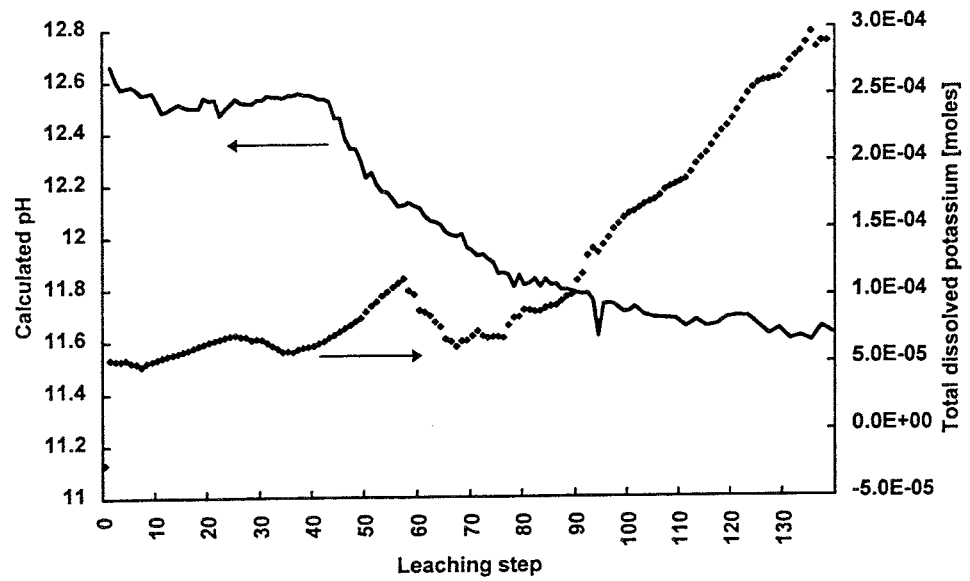
Figure 4-18. Total amount dissolved potassium from saline groundwater leached cement paste.
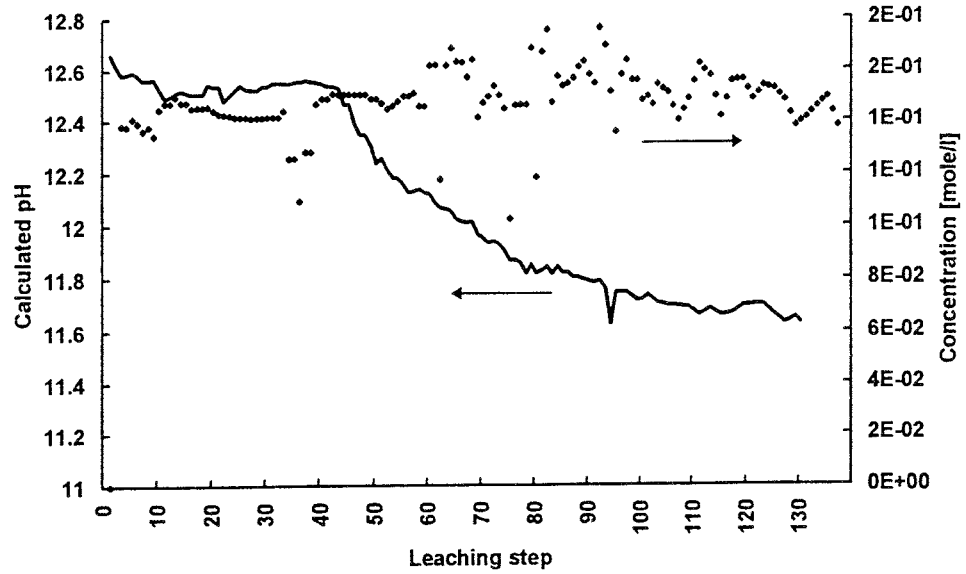
Figure 4-19. Concentration of sodium in saline groundwater leachate.
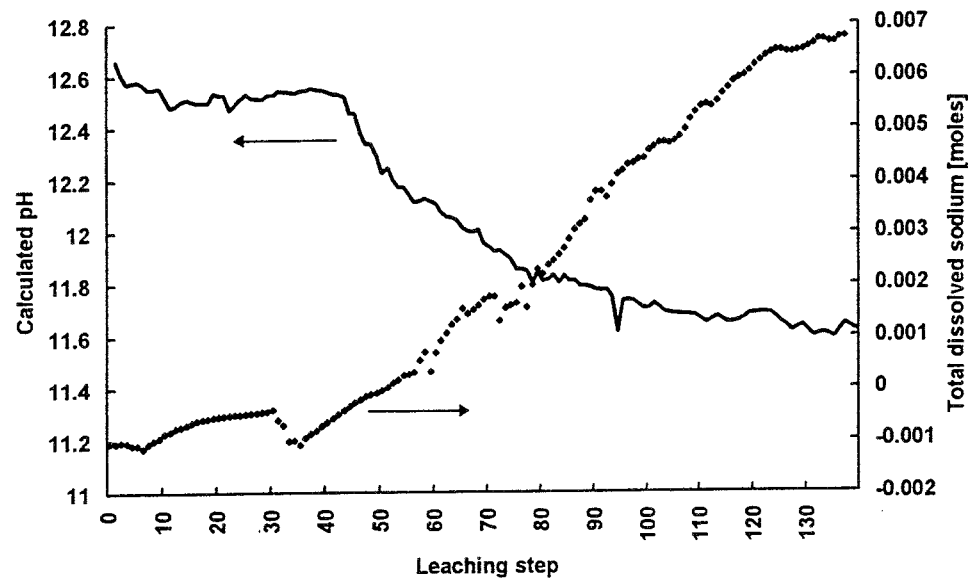
Figure 4-20. Total amount dissolved sodium from saline groundwater leached cement paste

Sulphate

Quite contrary to the non-saline groundwater samples, an continuous precipitation of sulphate is observed, *c.f.* Fig 4-21 and 4-22. This indicates formation of sulphate containing phases such as ettringite or thaumasite. However, this observation is contradicted by the solid phase analyses where a complete removal of surface ettringite was observed (Sect. 4.2).
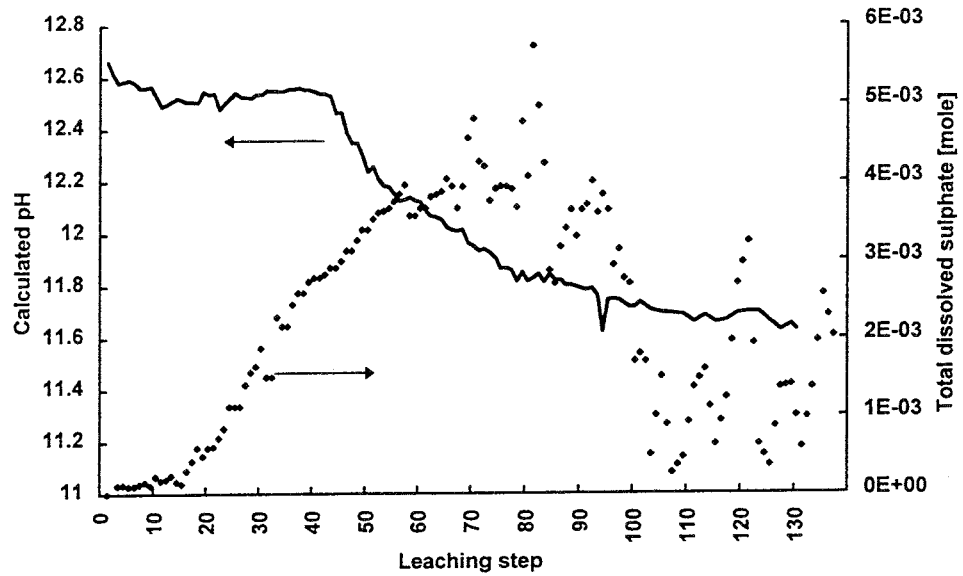
Figure 4-21. Concentration of sulphate in saline groundwater leachate.

Calcium
The leaching patterns of calcium look very much the same as for the non-saline groundwater leached samples, *c.f.* Figs. 4-23 and 4-24. The concentration in the leachate is however, about one order of magnitude higher in these samples. This is due to differences in the composition of the unreacted water, *c.f.* Table 3-1.

The total amount of dissolved calcium at leaching step 50 is about 5 mmoles which is 70% of that obtained in the non-saline groundwater experiment. The reason for this discrepancy could be analytical errors or differences in the
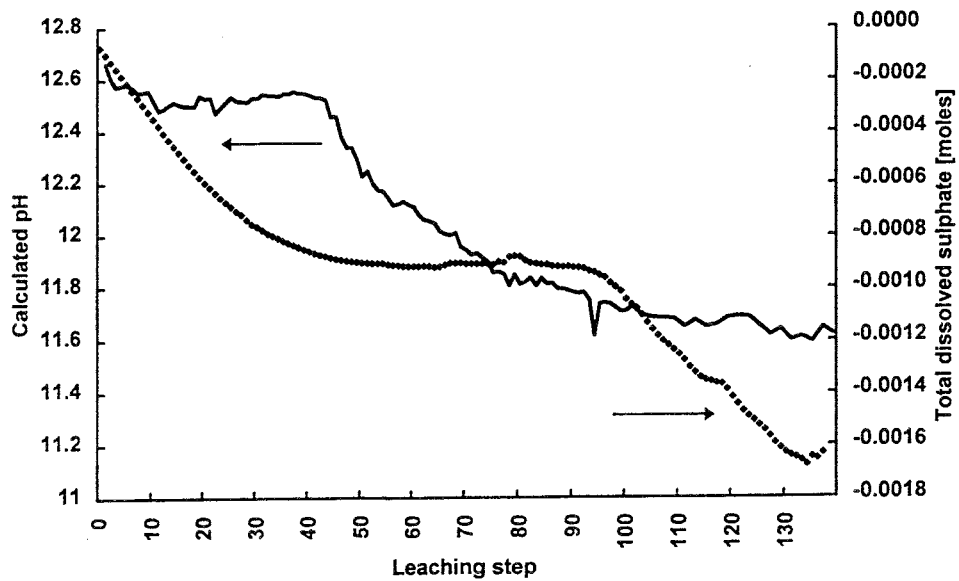
Figure 4-22. Total amount dissolved sulphate from saline groundwater leached cement paste.

samples. However, neither of these explanations seem likely since the analyses are rather reliable and the material is homogeneous (from the same piece of paste).
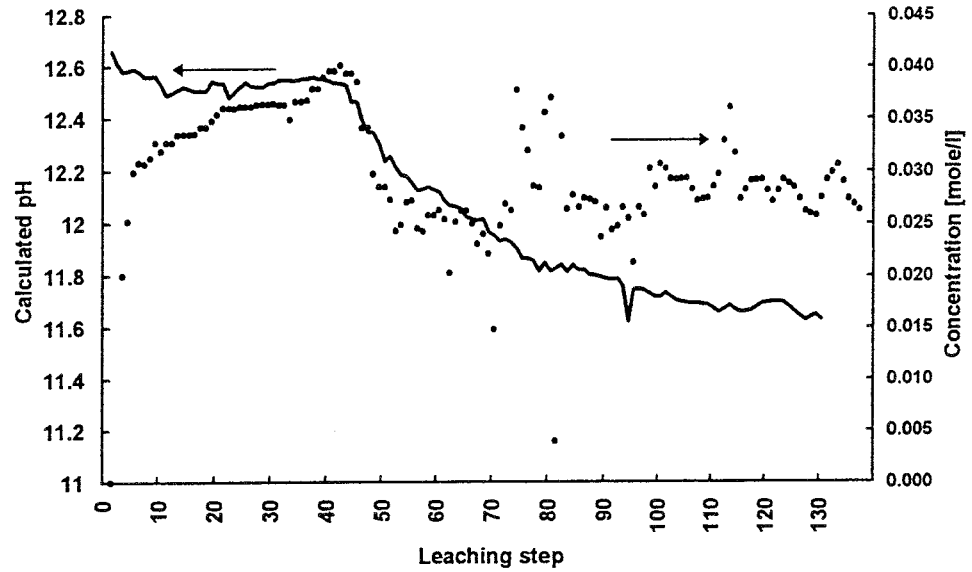
Figure 4-23. Concentration of calcium in saline groundwater leachate.
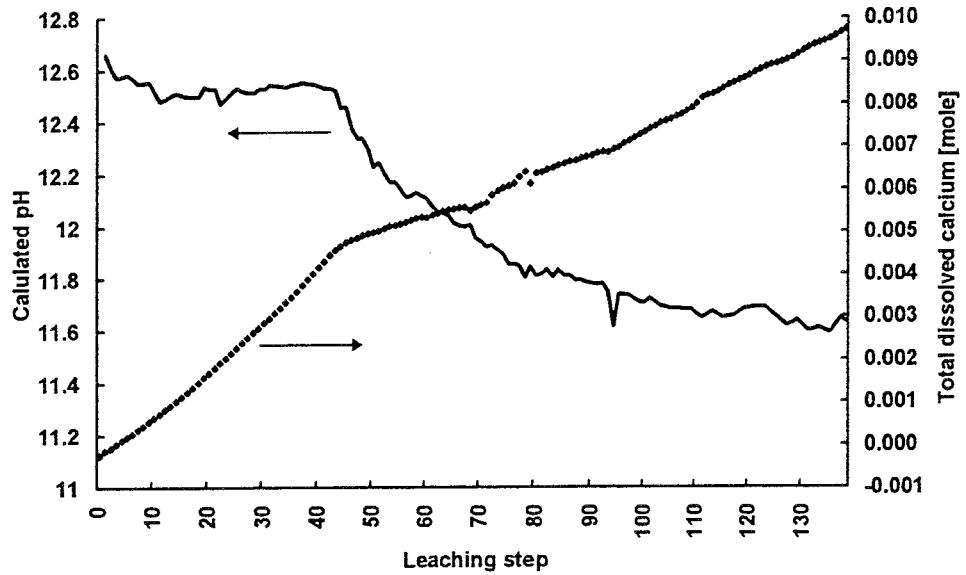
Figure 4-24. Total amount dissolved calcium from saline groundwater leached cement paste.
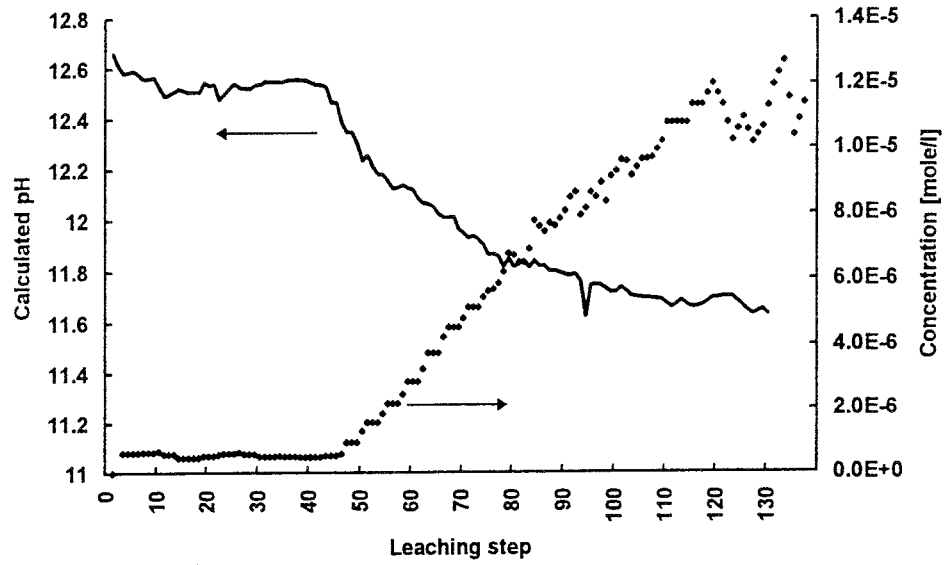
Figure 4-25. Concentration of silica in saline groundwater leachate.

Silica

The significant difference in the non-saline groundwater leached samples compared to saline experiments is that the unreacted water contained no silica c.f. Table 3-1. Consequently a continuous dissolution is observed c.f. Fig 4-25 and 4-26. The dissolution is accelerated when the pH is decreasing due to the removal of the portlandite.
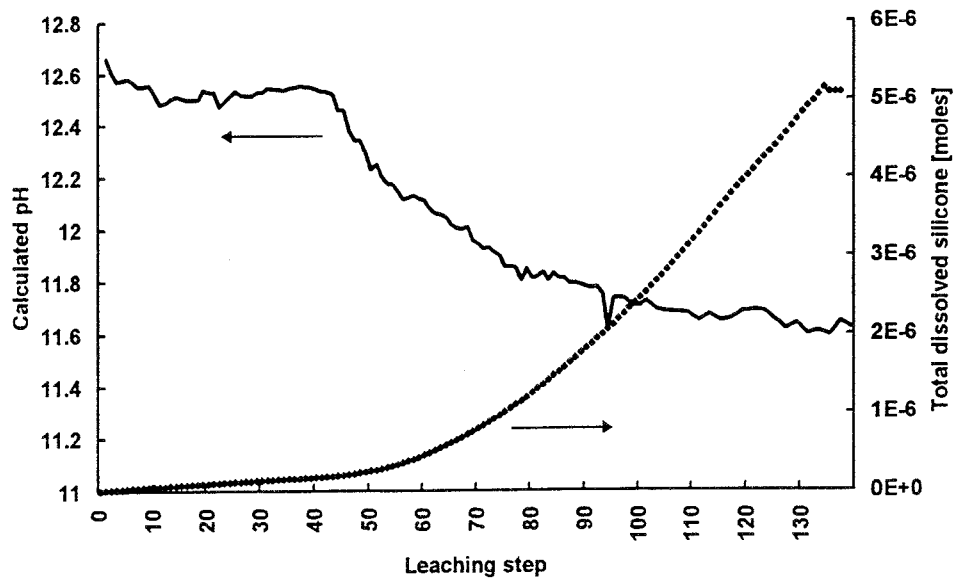
Figure 4-26. Total amount dissolved silica from saline groundwater leached cement paste.
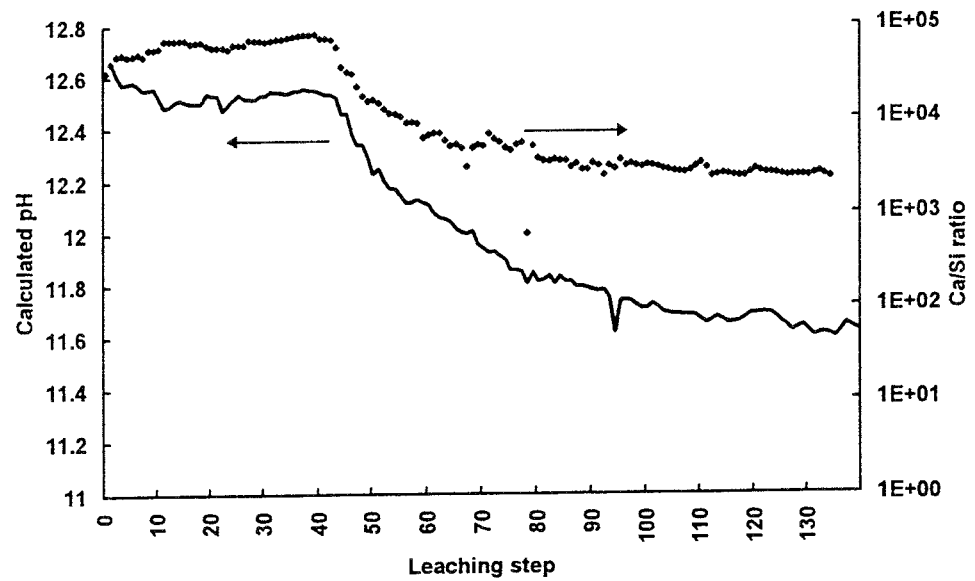
Figure 4-27. Ratio of the concentration ratio calcium to silica as a function of leaching steps.

Ca/Si ratio

As in non-saline groundwater leaching experiments, the correlation of the leaching patterns of calcium with silica (Ca concentration decreasing and Si increasing as a function of leaching steps) can be interpreted as calcium being exchanged for silica in the CSH giving lower Ca:Si ratios (*c.f.* Fig 4-27). This is quite obvious after leaching step 50 and can be interpreted as incongruent dissolution of CSH. This observation is supported by ATEM analysis of the solid leached samples where the Ca/Si ratio ranged from 1 to 1.7 with a majority below 1.5, *c.f.* Sect. 4.5. The unleached cement paste had a ratio of 1.48 to 1.73.

Figure 4-28. Concentration of aluminium in saline groundwater leachate.

Aluminium

Like the test with non-saline groundwater, aluminium was not analysed from the beginning of the experiment. In other words, it is impossible to calculate the massbalance for aluminium in the system. The concentration of aluminium is in the $\mu mole \cdot l^{-1}$ range, similar to the non-saline experiment, c.f. Fig 4-28.

4.2 RESULTS OF SOLID PHASE ANALYSIS

4.2.1 Unleached sample

The cement particles were typically 100μm in diameter and were generally subrounded to subangular (c.f. Plate 4-1). The external surfaces of the cement particles were coated by a calcium silicate hydrate (CSH) layer with short lath-to-rod-like morphology. A second type of CSH formed structureless patches up to 10 μm in diameter (c.f. Plate 4-2). Qualitative EXDA indicated that this phase had a lower Ca:Si ratio than the fibrous CSH noted. EXDA also indicated the presence of Fe and Mg in the stuctureless CSH phase.

In addition to the CSH phases, a calcium aluminosulphate phase was observed, c.f. Plate 4-3. This formed short euhedral to subhedral rods, up to 3 μm in length, with hexagonal cross-sections. Minor amounts of Si was detected in this compound. The morphology and qualitative chemistry suggested that this phase ought to be Si substituted ettringite, possibly forming a solid solution with thaumasite, a calcium silicate phosphate phase

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isostructural with ettringite. These ettringite rods could occasionally be found forming aggregates up to 4 μm across.

CSH formed the bulk of the cement matrix together with massive calcite. EXDA indicates that the CSH matrix also contained minor amounts of Mg, Al, Fe and trace amounts of K and S.

EXDA suggested that the CSH matrix had an approximate Ca:Si ratio of 3:2 compared to 4:1 for the fibrous CSH phase. However, it should be noted that the presence of finely intergrown and unresolved calcite in the underlying groundmass may have significantly affected the Ca:Si ratios determined by SEM-EXDA. Calcite also occurred as massive lumps up to 10μm across. These appeared to be post-date the development of the fibrous CSH.

4.2.2 Saline groundwater (NASK) leached sample

The most significant difference between the unreacted cement paste and the saline groundwater leached sample was the almost complete loss of the fibrous CSH that was present in the unleached sample (c.f. Plate 4-4). A fine "dustlike" coating was present on the cement paste particles. This appeared to be fragmented CSH fibres and ettringite rods. The dust appeared to be predominately composed of severely corroded and altered ettringite rods. EXDA indicated that only trace amounts of Al remained in the alteration product. Grain surfaces were composed of a calcium silicate, presumably hydrated with minor amounts of S and Cl. The semi-quantitative Ca:Si ratio, from EXDA, for this material was approximately 2:1, which indicated a possible increase in the proportion of Si within the CSH structure.

EXDA also indicates the presence of a minor Mg-rich CSH phase forming irregular and structureless patches up to 20 μm across. In addition, a minor structureless calcium silicosulphate phase, containing trace amounts of Al, occurred in the patches. This may represent an alteration product of ettringite.

4.2.3 Non-saline groundwater (Allard water) leached sample

This sample was similar to the saline groundwater leached sample. The fibrous CSH and ettringite rods covering the grain surfaces were completely removed (c.f. Plate 4-5). The fine relict coatings, seen in the saline groundwater leached sample, were absent in this sample, suggesting complete dissolution of ettringite. The host cement grains had a similar qualitative chemistry to the grains of the saline groundwater leached sample. Limited evidence from SEM indicates that structureless CSH formed an ir-regular coating on some grains (c.f. Plate 4-6). Calcite formed structureless

patches on a micron scale. EXDA indicates that the Mg-rich phases observed in the NASK samples were much more rare in this sample although minor amounts of Mg were sometimes detected in the structureless CSH material. In addition, a rare phase in which only Mg could be detected by EXDA, was also present. This material had a non-descript morphology and may represent products such as brucite ($Mg(OH)_2$, hydrotalcite ($Mg_6Al_2CO_3(OH)_{16} \cdot 4H_2O$) or magnesite ($MgCO_3$).
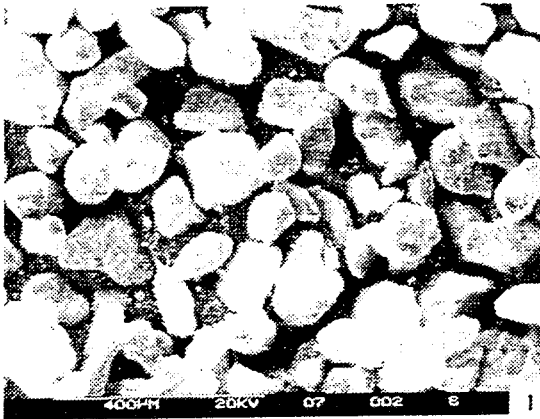
Plate 4-1. Secondary electron SEM photomicrograph showing typical grains that comprise the unreacted cement.
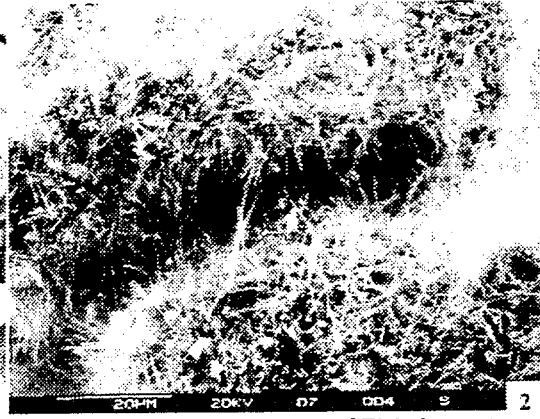
Plate 4-2. Secondary electron SEM photomicrograph of fibrous CSH and possibly later structureless CSH and portlandite which extensively coat all grain surfaces (unreacted cement).
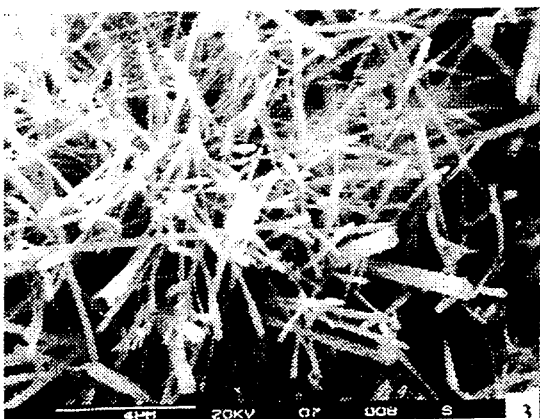
Plate 4-3. Secondary electron SEM photomicrograph of fibrous CSH and short ettringite rods with subhedral hexagonal cross-sections.
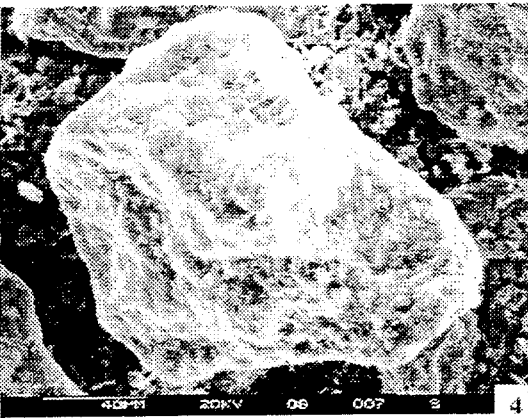
Plate 4-4. Secondary electron SEM photomicrograph of cement reacted with saline groundwater completely devoid of fibrous CSH and ettringite rods.
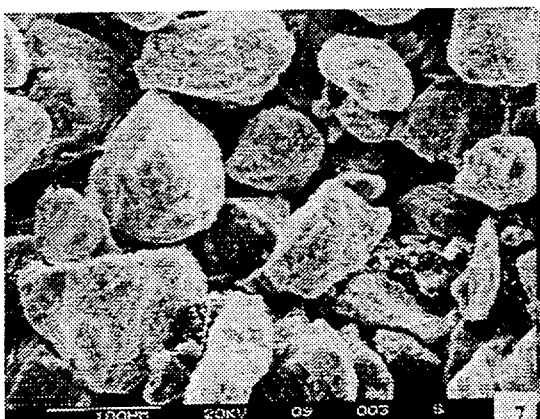
Plate 4-5. Secondary electron SEM photomicrograph showing typical grains that comprise the non-saline leached cement.
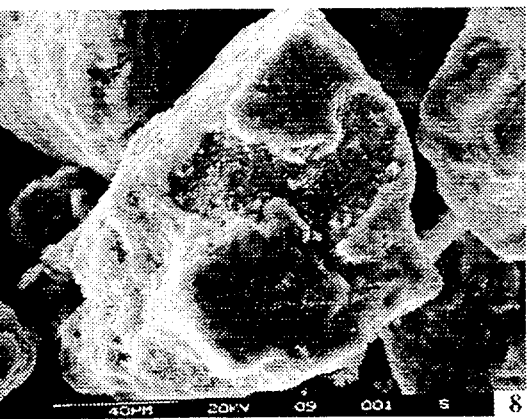
Plate 4-6. Secondary electron SEM photomicrograph of structureless CSH forming a coating of possibly calcite.

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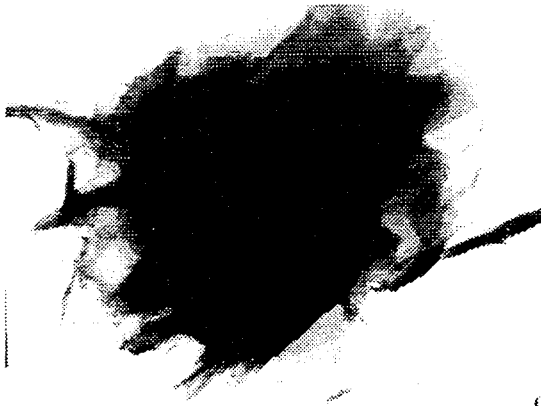
Plate 4-7 Transmission electron micrograph of ragged flaky CSH within the unreacted cement. Magnification x46 000.
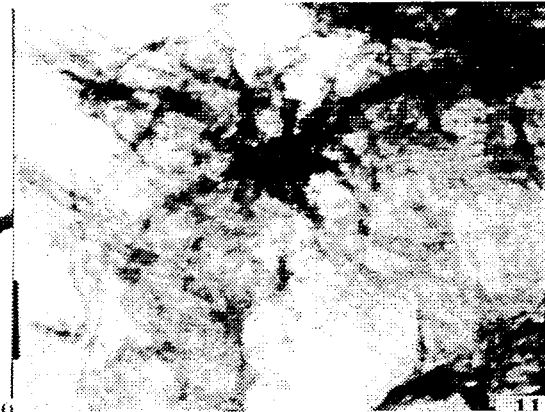
Plate 4-8 Transmission electron micrograph - of fibrous CSH. Analyses indicate this material has a Ca/Si ratio of less than 1.5 Magnification x 220000
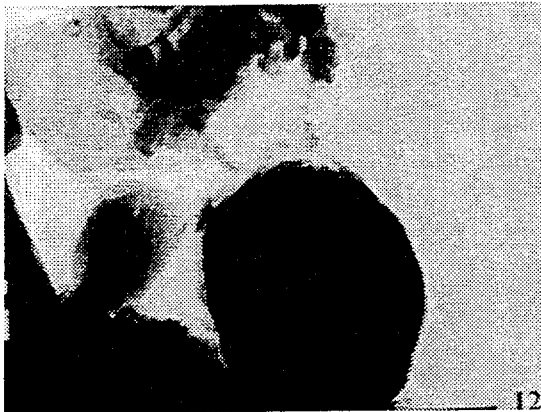
Plate 4-9 Transmission electron micrograph of denser CSH material with a Ca/Si ratio between 1.5 to 1.7. Magnification x80 000.

Plate 4-10 Transmission electron micrograph of bladed crystals of silica-substituted ettringite. Magnification x 13 000.

4.3   X-RAY DIFFRACTION

X-ray diffraction (XRD) interpretation of CSH is somewhat problematic. The principal d-spacings of CSH(A) are close to those of calcite. Also, the identification and distinction of crystalline calcium silicate hydrates by XRD is hampered due to the low "scattering power" of the H atom and because bound O, OH and H_2O contribute equally to the diffraction pattern (Lea, 1976).

The unleached cement material was determined by XRD to consist predominantly of portlandite and CSH(A) with minor amounts of calcite. CSH(A) has a very similar XRD pattern to the mineral scawtite ($7CaO\cdot6SiO_2\cdot CO_2\cdot2H_2O$) and is considered to have identical structure (Lea, 1976). This may suggest that the cement had been carbonated during setting and storing before the experiment started. In addition, both gypsum and the calcium silicate hydrate mineral hillebrandite ($Ca_2SiO_3(OH)_2$) were also tentatively identified.

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Portlandite had been removed from both the non-saline and saline ground-water leached samples. Also, hillebrandite and gypsum were identified in both the leached samples.

4.4 TGA (THERMOGRAVIMETRIC ANALYSIS)

The thermal analysis curves of the three samples were non-definitive in the sense that only one inflexion point was observed. The only definitive reaction in the samples was the loss of CO_2 above 600-650 °C due to the decomposition of calcite. The weight losses in all three samples were 20-24% which indicates that carbonation did not occur during the experiment and the carbonate present was in the original material.

4.5 ATEM (ANALYTICAL TRANSMISSION ELECTRON MICROSCOPY)

4.5.1 Unleached sample

Analyses of the fresh cement sample indicate the presence of CSH mineral with a Ca:Si ratio that varied from 1.48-1.73 *c.f.* Fig. 4-29.

This ratio is typical for the CSH (I and II) group of minerals. This ratio is also close to that of hillebrandite that was identified by XRD analysis. The material was composed of irregular masses of slightly flaky appearance with non-crystalline morphology (*c.f.* Plate 4-6). One analysis indicated the presence of a magnesium aluminate with a chemical formula close to M_3AH. Most analyses of material within the unleached cement showed that calcium aluminium silicosulphate minerals dominated. These minerals had a variable chemistry with silicate dominating in some and sulphate in others. The minerals were very hydrated and poorly crystalline. Silicosulphate minerals were also found and two different groups were identified. The first group was close to birunite ($Ca_{16}C_6Si_9SO_{49} \cdot 15H_2O$) and the second group was close to the natural mineral thaumasite ($(Ca_3Si(OH)_6 \cdot 12H_2O)SO_4CO_3$) *c.f.* Fig 4-30. Neither of these minerals contain aluminium in their ideal structure nor were they identified by XRD. The aluminium found was probably substituting silica which is possible in these minerals.

Figure 4-29. Ternary diagram for $Ca+Na_2+K_2$-Si-Al analyses of calcium hydrate phases from unreacted cement and cement reacted with non-saline groundwater. Locations of ideal C(A)SH minerals also plotted for reference.
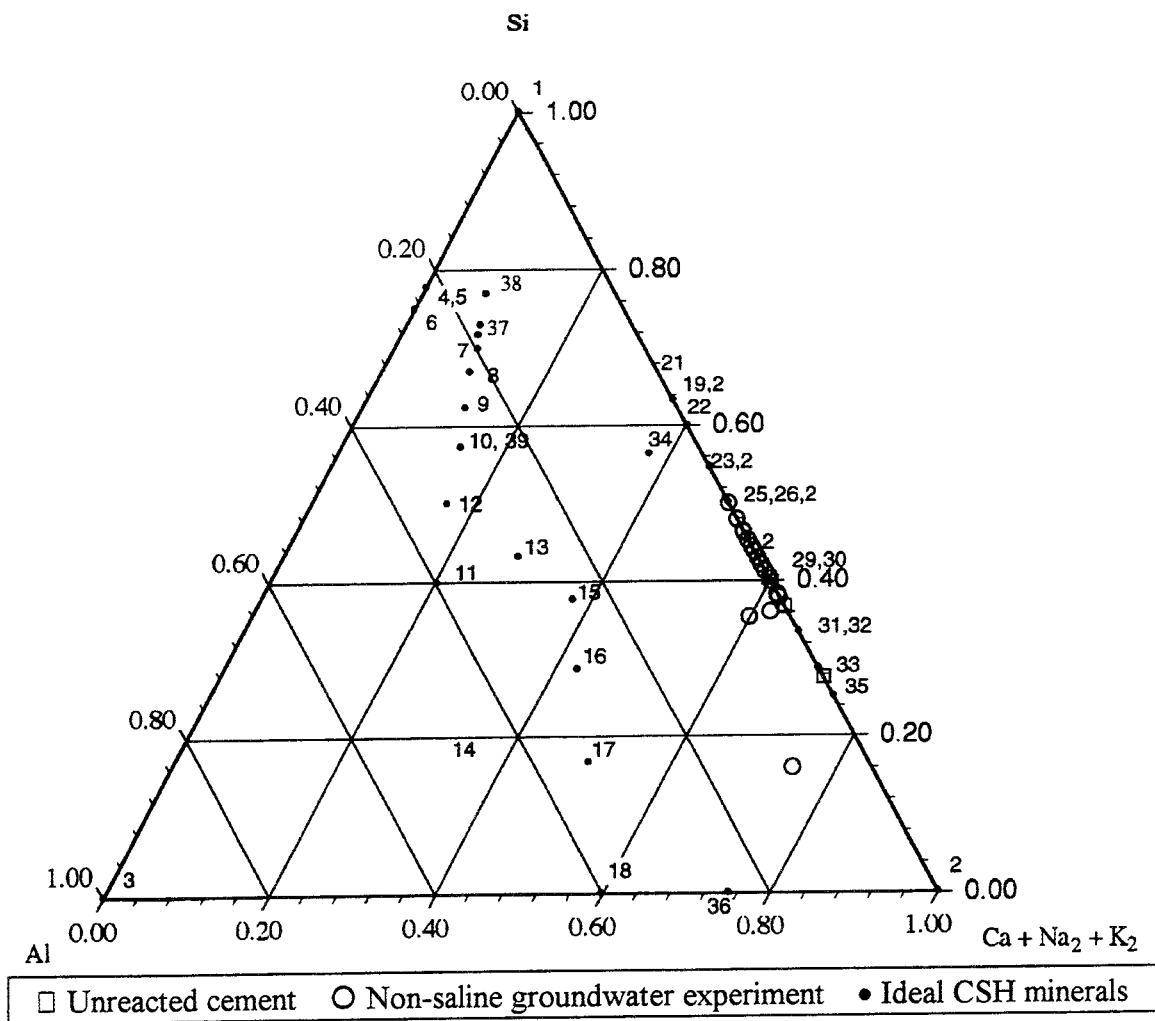
1	Quartz	14	Bicchulite	27	Suolinite
2	Portlandite	15	Grossular	28	Foshagite
3	Gibbsite	16	Hydrogrossular	29	Afwillite
4	Albite	17	Hydrogarnet	30	Jennite
5	Microline	18	Hydrogarnet	31	Hillebrandite
6	Stilbite (Na)	19	Nekoite	32	Dellaite
7	Stilbite (Ca)	20	Okenite	33	Reinhardbraunsite
8	Epstilbite	21	Truscottite	34	Tacharanite
9	Yugarawaralite	22	Gyrolite	35	Thaumasite
10	Laumontite	23	Tobermorite	36	Ettringite
11	Gismondine	24	Plombierite	37	Dachiardite
12	Scolecite	25	Xonolite	38	Mordenite
13	Prehnite	26	Rosenhahnite	39	Wairakite

SO4

1.00

0.80

0.60

0.40

0.20

0.00
Si4+

Al3+

□ Ca(±Mg,K)Al silicosulphates

○ Ca(±Mg,K,Fe)Al silicosulphates

• Ideal silicosulphate minerals

1 Thaumasite
2 Ettringite
3 Birunite
4 Latiumite
5 Meionite

Figure 4-30. Ternary diagram for Al-Si-SO₄ for analyses of calcium aluminium silicosulphate phases from unreacted cement. Locations of ideal $CaOAl_2O_3Y(Ca(SO_4,SiO_3)_x \cdot mH_2O$ minerals are also plotted for reference.

4.5.2   Saline groundwater leached sample

Two main phases were analysed in the cement paste leached with saline groundwater. The first was a calcium silicate hydrate phase that had a Ca:Si ratio range of 1.0 to 1.7 with a majority of observations below 1.5 c.f. Fig. 4-31. These observations support the assumption that the CSH belongs to the CSH(I) group of minerals with a chemical structure similar to tobermorite. The CSH with a ratio less than 1.5 had a predominantly fibrous to ribbon-like morphology that formed a tangled mat (c.f. Plate 4-8) whereas the CSH with a ratio between 1.5-1.7 had a structureless, dense rounded morphology (c.f. Plate 4-9).

Rod-like calcium aluminium silicosulphates were tightly clustered around ettringite and thaumasite (c.f. Plate 4-9). The formulae of this phase could be summarised as $(C,M)_3A \cdot 3Ca(SO_4, SiO_3)_{2.5-3.5} \cdot mH_2O$. The proportion of Mg in the phase varied from 1.3-7.9 wt%.
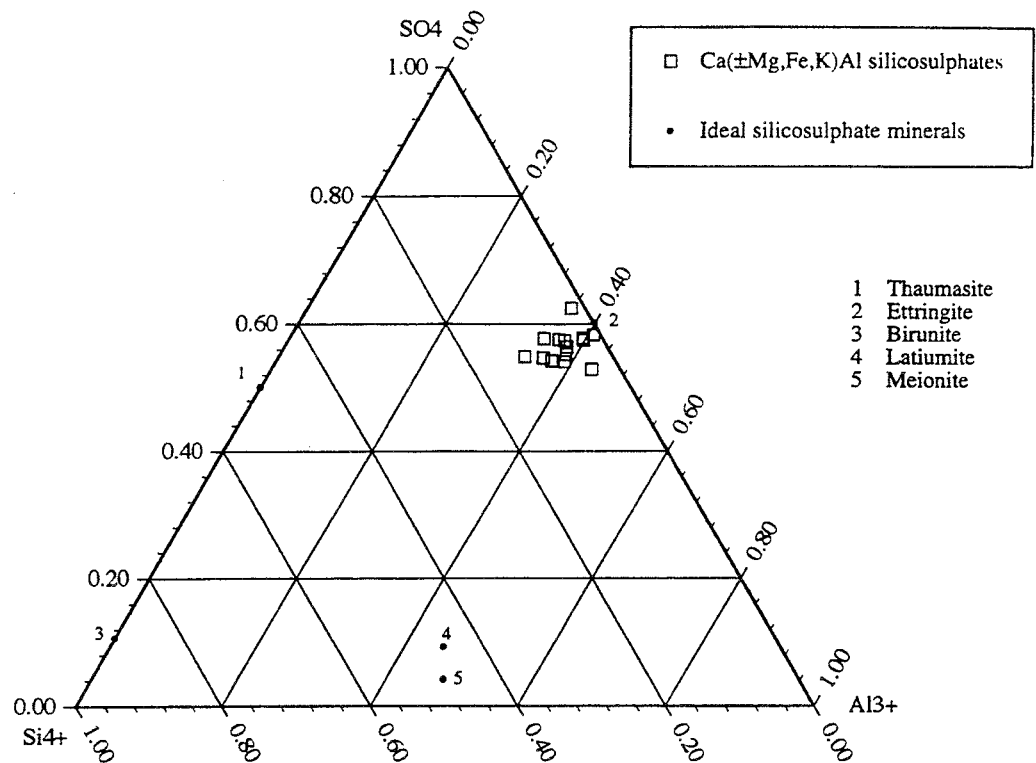
Figure 4-31. Ternary diagram for Al-Si-SO4 for analyses of calcium aluminium silicosulphate phases from cement reacted with saline groundwater. Locations of ideal $CaOAl_2O_3Y(Ca(SO_4,SiO_3))_x.mH_2O$ minerals are also plotted for reference.

4.5.3 Non-saline groundwater leached sample

Several different phases were analysed c.f. Fig 4-32. Calcium sulphate analyses indicate the presence of gypsum that was also tentatively identified by XRD. Analyses of a calcium potassium silicosulphate phase with bladed morphology (c.f. Plate 4-10) indicate a phase very similar to the silica substituted ettringite blades analysed in the saline groundwater leached sample. This phase had the unusual formula of $Ca_6K_{3.5-6}Si_{1.5-2.5}(SO_4)_{0-0.5}$ and was probably hydrated since it was very sensitive to the beam, probably due to the loss of water upon heating. Analyses also suggested the presence of a calcium aluminium silicosulphate phase, probably ettringite.

Masses of fibrous to ribbon-like CSH were observed, as in the saline groundwater leached sample, together with more structureless, denser CSH areas.

The cement matrix had similar morphologies in both the saline and non-saline groundwater samples.
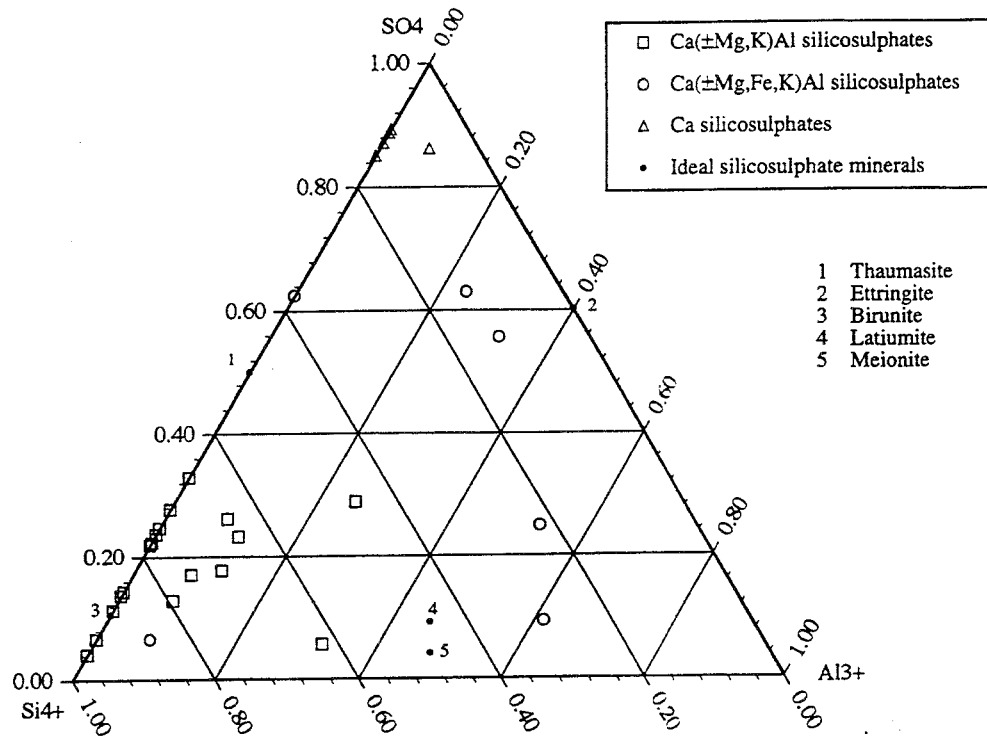
Figure 4-32. Ternary diagram for Al-Si-SO₄ for analyses of calcium aluminium silicosulphate phases from cement reacted with synthetic non-saline groundwater. Locations of ideal $CaOAl_2O_3Y(Ca(SO_4,SiO_3))_x.mH_2O$ minerals are also plotted for reference.

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5 DISCUSSION

Mineralogical and petrographical analyses established that the unleached cement consisted of portlandite, calcite, a matrix composed of CSH phase with a Ca.Si ratio of 1-1.3 and a second calcium silicate hydrate tentatively identified as hillbrandite (Ca:Si ratio of 1.5) plus minor amounts of calcium magnesium aluminium silicosulphate. Ettringite and thaumasite were also identified where ettringite was mostly found in the coating of the grains.

Most of the sulphate was bound in strongly hydrated calcium aluminium silicates. Gypsum had been tentatively identified but the charged imbalance of the ionic proportions indicates the presence of another cation. Analysis of the silicosulphate suggested that the phases had the general formula $(Ca_6Al_{0.5-1.5}(SO_4,SiO_3)_{2-3.3} \cdot mH_2O)$. Incorporation of hydroxide or carbonate would neutralise the apparent positive imbalance.

The leached samples that were mineralogically and petrographically analysed were leached 80 steps and had reached the point beyond where the hydroxide concentration started to decline from 0.03-0.04 M to one order of magnitude lower values. The initial interpretation was that the portlandite had been removed from the samples. This assumption was supported by the solid phase analyses where this mineral could not be identified.

The almost complete loss of fibrous CSH and ettringite at the particle surfaces in the leached samples could be caused by dissolution but also through grinding when agitating the samples. However, the particle size in all three samples were about 100μm in diameter indicating that the possible grinding had little effect apart from removing some coating. The size is also in accordance with the sieving when preparing the material. The uptake of sulphate is often a major concern when discussing the stability of cement. This uptake could lead to the formation of ettringite that causes expansion due to the high hydration number of the mineral. Constructions could deteriorate if excessive formation of ettringite would occur. In the experiments sulphate was taken up by the cement but there was no indication of formation of ettringite. The ettringite observed was formed before the experiments started (*i.e.* during setting). It should be clear that ettringite formation can occur but in more sulphate rich waters than was used in these experiments. Leach water analyses indicated an uptake of sulphate in the solid phase. It is likely that the sulphate was taken up by an anion substitution, possibly with carbonate. This seems reasonable since solid phase analyses indicated several silicosulphate phases (ettringite only being one) with various compositions.

The continuous leaching of calcium and uptake of silica observed in the leach waters is supported by the results from the solid phase analyses where several Ca-depleted CSH-phases were indicated with Ca:Si ratios ranging from 1.0 to 1.7.

There is no significant difference between the saline groundwater and the non-saline groundwater leached samples. The only clearly noticeable difference is the aluminium behaviour. The aluminium containing phases are more readily dissolved in non-saline groundwater.

In order to establish the time scale for the complete removal of portlandite, the following "back-of-the-envelope" calculation can be used. Assume the cement paste has a porosity of 15% and a density of 2700 kgm^{-3}. The pore volume of a 5g sample is approximately 0.3 ml and thus each leaching step corresponds to about 40 pore water exchanges. It has been calculated that in repository conditions, one pore water exchange takes about a thousand years (Lindgren et. al., 1994). As a result, 50 leaching steps (to remove portlandite) corresponds roughly to 2 million years. This figure is overestimated since it assumes constant porosity and complete pore water exchanges (which were not the case in the experiments). However, if all the material dissolved throughout the experiment (roughly 0.6 g) is added to the porosity, this would only lead to an increase of the porosity of about 12%. To be conservative, the experimental condition prolongs the life-time of the portlandite one order of magnitude. The time scale for which a pH of 12.5 (~0.03 M OH$^-$) could be expected inside or very close to the repository is more than 10^5 years. This is longer than the life-time for most radionuclides in the repository for long-lived intermediate level waste.

6   CONCLUSIONS

The most important conclusion from a safety assessment point of view is that a concrete construction gives a stable alkaline chemical environment for more than 10^5 years in a deep underground repository where the hydraulic gradients are small and the groundwater flow is slow. There is no point in considering a scenario where the cement has been leached to the degree where pH drops below approximately 12.5 and this is true both for non-saline and saline groundwater conditions.

Ettringite formation that causes expansion by binding large amounts of water (Lea, 1970) has not been observed in these experiments. However, the formation of ettringite could not be ruled out at higher sulphate concentrations (*e.g.* in sulphate rich bentonite porewaters or sulphate from degradation of cation exchange resins).

There is no evidence for excessive carbonation of the cement in the experiments. The calcite originates from setting and the storage of the cement and not from the leaching experiments.

7   ACKNOWLEDGEMENTS

REFERENCES

Atkins M, Glasser F P, Moroni L P, 1991. The long-term properties of cement and concretes. Mat. Res. Symp. 212.

Atkinson A, 1985. The time dependence of pH within a repository for radioactive waste disposal. AERE-R 11777, Harwell laboratory, Didcot

Baes C F, Mesmer R E, 1976. The hydrolysis of cations. John Wiley and Sons Inc

Berner U, 1992. Evolution of pore water chemistry during degradation of cement in a radioactive waste repository environment Waste Management, 12

Carberg S R, 1972. New Baltic manual with methods for sampling and analyses of physical, chemical and biological parameters. Int. Council for the Exploration of the Sea, Charlottenlund Slot, DK-2920 Charlottenlund, Denmark

Czernin W, 1969. Zementchemie für Bauingenieure (Swedish translation by Svenska Cementföreningen in Malmö: Cementkemi för byggare). Bauverlag GmbH, Wiesbaden-Berlin

Fujii K, Kondo W, 1981. Heterogeneous equilibrium of calcium silicate hydrate in water at 30°C. J. of Chem. Soc. Dalton, 2

Glasser F P, Angus M J, McCulloch C E, Macphee D, Rahman A A, 1985:1. The chemical environments in cement. Mat. Res. Symp. 44.

Glasser F P, Rahman A A,Macphee D, Angus M J, Atkins M, 1985:2. Immobilization of radioactive waste in cement-based matrices. University of Aberdeen, Dept. of chem., Meston Walk, Old Aberdeen, AB9 2UE, Scotland

Greenberg S A and Chang T N, 1965. Investigation of the colloidal hydrated calcium silicates-II. Solubility relationships in the calcium oxide-silica-water system at 25°C. J. of Phys. Chem. 69, 1965

Lachowski E E, Mohan K, Taylor, H F W, Moore A E, 1980. Analytical electron microscopy of cement pastes: II, Pastes of Portland cement and clinkers. J. Am. Ceram. Soc., 63, No 7-8

Lagerblad B, Trädgårdh J, 1995. Conceptual model for concrete long time degradation in a deep nuclear waste repository. SKB TR 95-21, Swedish Nuclear Fuel and Waste Management Co., Box 5864, S-102 40 Stockholm

Lea M F, 1970. The chemistry of cement and concrete. Edward Arnold Ltd, London

Lindgren M, Pers K, 1994. Radionuclide release from the near-field of SFL 3-5-A preliminary study, SKB AR 94-54, Swedish Nuclear Fuel and Waste Management Co., Box 5864, S-102 40 Stockholm

Neall F B, 1994. Modelling of the near-field chemistry of the SMA repository at the Wellenberg site. PSI Bericht No 94-18, Paul Scherrer Institut, Würenlingen and Villigen, CH-5232 Villigen

Savage D, Rochelle C A, 1993. Modelling reactions between cement pore fluids and rock: implications for porosity change. J. of Cont. Hydr., **13**

SR95, 1995. Mall för säkerhetsanalyser med beskrivande exempel. Swedish Nuclear Fuel and Waste Management Co., Box 5864, S-102 40 Stockholm

Trädgårdh B, 1996. Personal communication, Swedish cement and concrete research institute, Stockholm

APPENDIX

Leaching experiment with crushed cement paste

Non-saline groundwater

Results from water analyses

Concentrations in mole/l   Grey areas indicate average values (not analysed)

Allard	2.84E-03	1.00E-04	4.50E-04	1.97E-03	1.00E-04	2.10E-04	1.585E-06	
Leaching step	[Na]	[K]	[Ca]	[Cl]	[SO$_4$]	[SiO$_2$]	[OH]	[Al]
0								
1	4.75E-03	5.78E-03	2.08E-02	3.26E-04	3.30E-05	3.40E-06	0.0434195	
2	3.36E-03	1.85E-03	2.08E-02	6.68E-04	3.50E-05	2.50E-06	0.040048	
3	2.85E-03	6.67E-04	2.08E-02	9.77E-04	2.69E-05	2.60E-06	0.0402449	
4	2.72E-03	3.08E-04	2.03E-02	1.22E-03	2.39E-05	3.00E-06	0.038377	
5	2.66E-03	1.64E-04	1.98E-02	1.57E-03	2.24E-05	2.90E-06	0.0407653	
6	2.60E-03	1.31E-04	1.94E-02	1.47E-03	2.15E-05	2.50E-06	0.0404882	
7	2.62E-03	1.05E-04	1.94E-02	1.61E-03	2.34E-05	2.60E-06	0.0405223	
8	2.97E-03	1.37E-04	1.99E-02	1.74E-03	2.52E-05	2.30E-06	0.0395076	
9	2.90E-03	1.18E-04	1.98E-02	1.72E-03	2.65E-05	2.20E-06	0.0403051	
10	2.59E-03	1.23E-04	2.00E-02	1.68E-03	3.02E-05	2.20E-06	0.0397582	
11	2.59E-03	1.11E-04	1.96E-02	1.70E-03	1.87E-05	2.60E-06	0.0394956	
12	2.67E-03	1.19E-04	1.91E-02	1.71E-03	2.18E-05	2.60E-06	0.0397458	
13	2.78E-03	1.32E-04	1.99E-02	1.76E-03	1.95E-05	4.20E-06	0.0397799	
14	2.64E-03	1.34E-04	2.00E-02	1.57E-03	2.97E-05	3.80E-06	0.040358	
15	2.62E-03	1.15E-04	1.97E-02	1.60E-03	3.07E-05	2.90E-06	0.0394842	
16	2.75E-03	1.17E-04	1.97E-02	1.58E-03	3.19E-05	2.30E-06	0.0393238	
17	2.57E-03	1.22E-04	2.06E-02	1.81E-03	2.12E-05	2.50E-06	0.0392938	
18	2.56E-03	1.21E-04	2.07E-02	1.86E-03	2.00E-05	2.70E-06	0.0387705	
19	2.63E-03	4.95E-04	1.90E-02	1.73E-03	2.13E-05	2.95E-06	0.0377771	
20	2.76E-03	3.21E-04	1.86E-02	1.82E-03	2.16E-05	3.20E-06	0.037628	
21	2.88E-03	1.48E-04	1.83E-02	1.90E-03	2.19E-05	2.37E-06	0.0366339	2.48E-06
22	2.99E-03	1.45E-04	1.81E-02	2.03E-03	2.25E-05	6.02E-06	0.0362855	1.708E-06
23	2.99E-03	1.45E-04	1.81E-02	2.03E-03	2.25E-05	9.67E-06	0.0362855	2.19E-06
24	2.99E-03	1.45E-04	1.81E-02	2.03E-03	2.25E-05	6.47E-06	0.0348941	1.37E-06
25	3.10E-03	1.42E-04	1.79E-02	2.15E-03	2.30E-05	3.27E-06	0.0359372	7.451E-06
26	2.88E-03	1.19E-04	1.87E-02	2.01E-03	2.66E-05	3.07E-06	0.036329	3.653E-06
27	2.88E-03	1.19E-04	1.87E-02	1.97E-03	2.79E-05	3.07E-06	0.0364026	2.722E-06
28	2.66E-03	9.70E-05	1.95E-02	1.90E-03	2.37E-05	2.87E-06	0.0364762	3.804E-06
29	2.65E-03	9.90E-05	1.95E-02	1.88E-03	2.27E-05	2.67E-06	0.0377569	2.571E-06
30	2.65E-03	9.90E-05	1.95E-02	1.88E-03	2.27E-05	2.67E-06	0.0377569	3.628E-06
31	2.64E-03	1.01E-04	1.94E-02	1.86E-03	2.17E-05	2.47E-06	0.0390377	2.143E-06
32	2.75E-03	1.16E-04	1.95E-02	1.96E-03	2.64E-05	2.62E-06	0.0392649	2.219E-06
33	2.75E-03	1.16E-04	1.95E-02	1.96E-03	2.64E-05	2.62E-06	0.0392649	1.917E-06
34	2.86E-03	1.31E-04	1.96E-02	2.05E-03	3.10E-05	2.77E-06	0.039492	2.395E-06
35	2.86E-03	1.38E-04	1.98E-02	1.91E-03	2.48E-05	2.80E-06	0.0397899	2.018E-06
36	2.86E-03	1.38E-04	1.98E-02	1.91E-03	2.48E-05	2.80E-06	0.0397899	2.672E-06
37	2.86E-03	1.45E-04	2.00E-02	1.77E-03	1.86E-05	2.83E-06	0.0400878	2.068E-06
38	2.90E-03	1.46E-04	1.97E-02	1.70E-03	2.23E-05	2.95E-06	0.0395758	2.395E-06
39	2.90E-03	1.46E-04	1.97E-02	1.70E-03	2.23E-05	2.95E-06	0.0395758	2.496E-06
40	2.94E-03	1.48E-04	1.95E-02	1.62E-03	2.60E-05	3.07E-06	0.0390638	2.848E-06
41	2.94E-03	1.45E-04	2.02E-02	1.74E-03	2.43E-05	3.12E-06	0.039207	5.816E-06
42	2.94E-03	1.45E-04	2.02E-02	1.74E-03	2.43E-05	3.12E-06	0.039207	2.194E-06
43	2.94E-03	1.43E-04	2.10E-02	1.85E-03	2.27E-05	3.17E-06	0.0393502	2.345E-06
44	2.99E-03	1.52E-04	2.06E-02	1.87E-03	2.38E-05	3.15E-06	0.0388161	2.294E-06
45	2.99E-03	1.52E-04	2.06E-02	1.87E-03	2.38E-05	3.13E-06	0.0388161	1.867E-06

Concentrations in mole/l			Grey areas indicate average values (not analysed)					
Allard	2.84E-03	1.00E-04	4.50E-04	1.97E-03	1.00E-04	2.10E-04	1.585E-06	
Leaching step	[Na]	[K]	[Ca]	[Cl]	[SO$_4$]	[SiO$_2$]	[OH]	[Al]
46	3.04E-03	1.62E-04	2.03E-02	1.89E-03	2.48E-05	3.00E-06	0.0382819	1.822E-06
47	3.04E-03	1.63E-04	1.77E-02	2.01E-03	2.82E-05	3.60E-06	0.0335422	3.89E-06
48	3.04E-03	1.63E-04	1.77E-02	2.01E-03	2.82E-05	4.42E-06	0.0335422	4.393E-06
49	3.03E-03	1.65E-04	1.50E-02	2.12E-03	3.16E-05	5.23E-06	0.0288024	1.102E-05
50	2.75E-03	1.70E-04	1.27E-02	1.87E-03	4.32E-05	1.01E-05	0.0247693	8.158E-06
51	3.04E-03	1.94E-04	1.28E-02	2.18E-03	4.59E-05	5.93E-06	0.0250288	8.051E-06
52	2.99E-03	1.68E-04	1.23E-02	2.15E-03	4.59E-05	9.00E-06	0.0227071	7.972E-06
53	2.95E-03	1.55E-04	1.18E-02	2.09E-03	5.37E-05	3.73E-05	0.0220505	5.427E-06
54	2.80E-03	1.56E-04	1.06E-02	2.18E-03	6.37E-05	9.37E-05	0.0203335	8.184E-06
55	2.92E-03	1.55E-04	1.01E-02	2.16E-03	6.83E-05	1.20E-05	0.0192376	1.291E-05
56	3.42E-03	1.07E-04	9.61E-03	2.25E-03	7.69E-05	4.95E-06	0.0182103	1.038E-05
57	3.42E-03	1.07E-04	9.61E-03	2.25E-03	7.69E-05	6.63E-06	0.0178348	1.272E-05
58	3.91E-03	5.80E-05	9.13E-03	2.35E-03	8.54E-05	8.48E-06	0.0178164	1.525E-05
59	3.10E-03	2.62E-04	1.00E-02	2.80E-03	1.05E-04	7.45E-06	0.0171284	1.31E-05
60	4.27E-03	5.71E-05	9.35E-03	2.32E-03	1.16E-04	8.44E-06	0.0160665	1.358E-05
61	3.86E-03	4.25E-05	8.34E-03	2.29E-03	1.20E-04	3.22E-05	0.0154718	1.601E-05
62	3.95E-03	4.86E-05	7.91E-03	2.02E-03	1.25E-04	9.36E-06	0.014966	1.596E-05
63	3.74E-03	4.39E-05	7.71E-03	2.04E-03	1.52E-04	1.12E-05	0.0145034	1.802E-05
64	3.90E-03	4.60E-05	7.52E-03	1.99E-03	1.47E-04	1.55E-05	0.0136859	1.816E-05
65	3.77E-03	2.48E-04	7.19E-03	2.02E-03	1.67E-04	4.73E-05	0.013299	1.596E-05
66	3.90E-03	4.38E-05	6.79E-03	2.17E-03	1.90E-04	1.51E-05	0.0130675	1.668E-05
67	3.35E-03	5.44E-05	6.49E-03	2.16E-03	2.90E-04	1.56E-05	0.0127241	1.778E-05
68	3.38E-03	4.61E-05	6.27E-03	2.17E-03	2.41E-04	1.46E-05	0.012568	1.415E-05
69	3.38E-03	4.98E-05	6.10E-03	2.21E-03	2.70E-04	1.45E-05	0.0116795	1.644E-05
70	3.53E-03	4.33E-05	6.03E-03	2.36E-03	3.06E-04	1.62E-05	0.0119494	2.093E-05
71	3.46E-03	4.00E-05	5.71E-03	2.19E-03	2.89E-04	1.60E-05	0.0113604	1.224E-05
72	3.39E-03	6.54E-05	6.00E-03	2.15E-03	2.44E-04	1.82E-05	0.0115759	3.026E-07
73	3.32E-03	9.07E-05	6.28E-03	2.10E-03	2.00E-04	2.04E-05	0.0117915	2.16E-05
74	3.27E-03	1.06E-04	5.80E-03	2.03E-03	2.00E-04	2.08E-05	0.0112	2.002E-05
75	3.12E-03	8.13E-05	5.26E-03	1.90E-03	2.00E-04	2.27E-05	0.0103921	2.403E-05
76	3.20E-03	9.45E-05	5.33E-03	1.90E-03	2.00E-04	2.45E-05	0.0099665	2.752E-05
77	3.03E-03	1.97E-04	5.07E-03	1.83E-03	3.00E-04	3.36E-05	0.009548	1.85E-05
78	2.99E-03	1.85E-04	4.97E-03	1.83E-03	3.00E-04	3.52E-05	0.009637	3.927E-05
79	3.00E-03	1.00E-04	4.57E-03	1.70E-03	4.00E-04	2.58E-05	0.009215	3.048E-05
80	3.30E-03	1.67E-04	5.07E-03	1.70E-03	4.33E-04	2.65E-05	0.009017	1.573E-05
81	3.10E-03	1.33E-04	4.60E-03	1.80E-03	3.67E-04	2.80E-05	0.008676	1.539E-05
82	2.95E-03	1.00E-04	4.50E-03	2.40E-03	3.00E-04	3.03E-05	0.008802	1.883E-05
83	3.05E-03	1.00E-04	4.50E-03	2.35E-03	4.00E-04	3.04E-05	0.009054	2.561E-05
84	3.10E-03	1.00E-04	4.45E-03	2.35E-03	4.75E-04	3.82E-05	0.009314	1.659E-05
85	3.20E-03	2.00E-04	4.50E-03	2.35E-03	4.75E-04	4.03E-05	0.009092	1.467E-05
86	2.30E-03	1.00E-04	3.20E-03	2.35E-03	5.50E-04	3.22E-05	0.008247	1.897E-05
87	2.50E-03	1.50E-04	3.00E-03	2.15E-03	6.00E-04	3.42E-05	0.008194	1.626E-05
88	2.20E-03	2.00E-04	3.10E-03	2.90E-03	7.50E-04	3.65E-05	0.008066	1.641E-05
89	2.10E-03	1.50E-04	3.05E-03	2.80E-03	7.00E-04	3.83E-05	0.007794	3.286E-05
90	2.40E-03	2.50E-04	3.15E-03	2.30E-03	7.00E-04	4.02E-05	0.00786	1.984E-05
91	2.25E-03	2.00E-04	3.50E-03	2.35E-03	6.00E-04	4.29E-05	0.007772	1.83E-05
92	2.85E-03	2.50E-04	2.90E-03	2.45E-03	5.50E-04	4.30E-05	0.007624	2.125E-05
93	3.00E-03	3.00E-04	2.75E-03	2.40E-03	6.00E-04	4.61E-05	0.0072	1.781E-05
94	3.25E-03	2.00E-04	3.00E-03	1.70E-03	6.00E-04	4.71E-05	0.00622	1.888E-05

Concentrations in mole/l			Grey areas indicate average values (not analysed)					
Allard	2.84E-03	1.00E-04	4.50E-04	1.97E-03	1.00E-04	2.10E-04	1.585E-06	
Leaching step	[Na]	[K]	[Ca]	[Cl]	[SO$_4$]	[SiO$_2$]	[OH]	[Al]
95	3.60E-03	2.00E-04	3.55E-03	1.65E-03	6.00E-04	4.88E-05	0.007127	1.81E-05
96	2.95E-03	1.50E-04	3.35E-03	2.40E-03	5.00E-04	4.81E-05	0.007022	1.849E-05
97	3.20E-03	2.00E-04	3.90E-03	2.30E-03	5.50E-04	5.35E-05	0.006515	1.907E-05
98	2.70E-03	2.00E-04	3.40E-03	2.35E-03	6.00E-04	5.17E-05	0.00675	2.018E-05
99	2.85E-03	2.00E-04	3.05E-03	2.85E-03	6.50E-04	5.40E-05	0.006411	2.193E-05
100	3.00E-03	2.00E-04	3.05E-03	3.20E-03	6.00E-04	5.60E-05	0.006442	2.134E-05
101	2.45E-03	2.00E-04	3.15E-03	2.40E-03	8.00E-04	5.56E-05	0.006752	2.164E-05
102	2.63E-03	2.00E-04	3.23E-03	2.35E-03	8.75E-04	5.82E-05	0.006504	
103	2.80E-03	2.00E-04	3.30E-03	2.30E-03	9.50E-04	5.97E-05	0.006256	2.159E-05
104	2.70E-03	2.00E-04	3.10E-03	2.15E-03	8.75E-04	6.08E-05	0.0060745	
105	2.60E-03	2.00E-04	2.90E-03	2.00E-03	8.00E-04	8.78E-05	0.005893	2.222E-05
106	2.70E-03	2.00E-04	3.08E-03	1.95E-03	1.10E-03	8.78E-05	0.005868	
107	2.80E-03	2.00E-04	3.25E-03	1.90E-03	1.40E-03	1.15E-04	0.005843	2.159E-05
108	2.90E-03	2.00E-04	3.13E-03	2.05E-03	1.45E-03	1.16E-04	0.005522	
109	3.05E-03	2.00E-04	3.00E-03	2.20E-03	1.50E-03	1.02E-04	0.005201	
110	3.08E-03	2.00E-04	3.25E-03	2.15E-03	1.35E-03	9.66E-05	0.0053375	
111	3.10E-03	2.00E-04	3.50E-03	2.10E-03	1.20E-03	8.97E-05	0.005474	
112	2.98E-03	2.25E-04	3.23E-03	2.03E-03	1.18E-03	1.02E-04	0.005518	
113	2.85E-03	2.50E-04	2.95E-03	1.95E-03	1.15E-03	9.63E-05	0.005562	
114	2.98E-03	2.50E-04	2.85E-03	1.95E-03	8.75E-04	1.08E-04	0.005254	
115	3.10E-03	2.50E-04	2.75E-03	1.95E-03	6.00E-04	1.35E-04	0.004946	
116	3.20E-03	2.25E-04	2.78E-03	2.03E-03	7.50E-04	1.41E-04	0.005126	
117	3.30E-03	2.00E-04	2.80E-03	2.10E-03	9.00E-04	1.09E-04	0.005306	
118	3.18E-03	2.00E-04	2.95E-03	2.20E-03	1.20E-03	1.15E-04	0.005271	
119	3.05E-03	2.00E-04	3.10E-03	2.30E-03	1.50E-03	1.06E-04	0.005236	
120	2.95E-03	2.00E-04	3.05E-03	2.43E-03	1.63E-03	1.26E-04	0.0053065	
121	2.85E-03	2.00E-04	3.00E-03	2.55E-03	1.75E-03	1.13E-04	0.005377	
122	3.23E-03	2.25E-04	2.88E-03	2.68E-03	1.50E-03	1.35E-04	0.005349	
123	3.60E-03	2.50E-04	2.75E-03	2.80E-03	1.35E-03	2.37E-05	0.005321	
124	3.43E-03	2.25E-04	2.65E-03	2.85E-03	1.33E-03	2.72E-05	0.004875	
125	3.25E-03	2.00E-04	2.55E-03	2.90E-03	1.30E-03	3.06E-05	0.004429	
126	3.30E-03	2.00E-04	2.43E-03	2.95E-03	1.08E-03	3.24E-05	0.004478	
127	3.35E-03	2.00E-04	2.30E-03	3.00E-03	8.50E-04	3.41E-05	0.004527	
128	3.50E-03	2.00E-04	2.48E-03	2.95E-03	9.75E-04	3.64E-05	0.0043805	
129	3.70E-03	2.00E-04	2.65E-03	2.90E-03	1.10E-03	3.87E-05	0.004234	
130	3.58E-03	2.50E-04	2.50E-03	2.68E-03	1.15E-03	3.94E-05	0.00422	
131	3.45E-03	3.00E-04	2.35E-03	2.45E-03	1.20E-03	4.01E-05	0.004206	
132	3.15E-03	2.75E-04	2.25E-03	2.23E-03	1.18E-03	3.87E-05	0.004203	
133	2.85E-03	2.50E-04	2.15E-03	2.00E-03	1.15E-03	3.72E-05	0.0042	
134	2.98E-03	2.50E-04	2.08E-03	1.93E-03	1.10E-03	3.84E-05	0.004041	
135	3.10E-03	2.50E-04	2.00E-03	1.85E-03	1.05E-03	3.95E-05	0.003882	
136	3.04E-03	1.40E-04	2.27E-03	1.81E-03	1.14E-03	1.06E-04	0.0040075	
137	2.75E-03	1.80E-04	2.27E-03	1.82E-03	1.53E-03	1.26E-04	0.004133	
138	3.13E-03	1.80E-04	2.17E-03	1.82E-03	1.03E-03	1.13E-04	0.0043875	
139	3.18E-03	2.20E-04	2.23E-03	1.81E-03	1.65E-03	1.35E-04	0.004642	
140		2.00E-04	2.18E-03	0.001805	1.34E-03	1.30E-04	0.0044969	
141	3.27E-03	1.80E-04	2.12E-03	1.80E-03	1.03E-03	1.26E-04	0.0043518	
142		2.25E-04	2.15E-03	1.89E-03	9.45E-04	1.20E-04	0.0042706	
143	3.13E-03	2.70E-04	2.17E-03	1.97E-03	8.60E-04	1.14E-04	0.0041894	

Concentrations in mole/l				Grey areas indicate average values (not analysed)				
Allard	2.84E-03	1.00E-04	4.50E-04	1.97E-03	1.00E-04	2.10E-04	1.585E-06	
Leaching step	[Na]	[K]	[Ca]	[Cl]	[SO$_4$]	[SiO$_2$]	[OH]	[Al]
144		1.95E-04	2.31E-03	1.98E-03	8.55E-04	1.23E-04	0.0041882	
145	2.90E-03	1.20E-04	2.44E-03	1.98E-03	8.50E-04	1.31E-04	0.0042	
146		1.50E-04	2.41E-03	2.03E-03	8.28E-04	1.35E-04	0.0041585	
147	3.34E-03	1.80E-04	2.37E-03	2.07E-03	8.05E-04	1.39E-04	0.00413	
148								
149								

Leaching experiment with crushed cement paste							
Saline groundwater							

Results from water analyses

Concentrations in mole/l				Grey areas indicate average values (not analysed)			
NASK	0.14	0.002046	0.01995	0.003954	0	1.58E-06	
Leaching step	[Na]	[K]	[Ca]	[SO4]	[SiO2]	[OH]	[Al]
0							
1	0.138333333	0.00775	0.02	0.000111	6.3E-07	0.0504	
2	0.138	0.004263333	0.0252	0.000118	6.3E-07	0.0448	
3	0.141	0.002923333	0.029833333	0.0000995	6.3E-07	0.0422	
4	0.139333333	0.00247	0.0308	0.000103	6.3E-07	0.0428	
5	0.136333333	0.002043333	0.030633333	0.000129	6.57E-07	0.0434	
6	0.138	0.00198	0.0312	0.00015	6.57E-07	0.0422	
7	0.134333333	0.00182	0.032666667	0.00011	6.57E-07	0.0406	
8	0.144666667	0.002176667	0.0319	0.000224	6.84E-07	0.0406	
9	0.147166667	0.002203333	0.032666667	0.000174	5.85E-07	0.0412	
10	0.147166667	0.002203333	0.032666667	0.000188	5.85E-07	0.037848	
11	0.149666667	0.00223	0.033433333	0.000236	5.85E-07	0.034634	
12	0.1475	0.002206667	0.0335	0.00016	4.86E-07	0.035313	
13	0.1475	0.002206667	0.0335	0.000132	4.86E-07	0.036332	
14	0.145333333	0.002183333	0.033566667	0.000299	4.86E-07	0.037351	
15	0.1455	0.002211667	0.034166667	0.000421	4.86E-07	0.036754	
16	0.1455	0.002211667	0.034166667	0.000593	4.86E-07	0.036158	
17	0.145666667	0.00224	0.034766667	0.000487	5.34E-07	0.036183	
18	0.144333333	0.002245	0.035383333	0.00059	5.34E-07	0.036208	
19	0.143	0.00225	0.036	0.000607667	5.34E-07	0.039782	
20	0.142666667	0.002238333	0.035983333	0.000723333	5.82E-07	0.038788	
21	0.142333333	0.002226667	0.035966667	0.000839	6.18E-07	0.039136	1.15E-06
22	0.141666667	0.002201667	0.036133333	0.0011195	6.18E-07	0.0341	9.84E-07
23	0.141666667	0.002201667	0.036133333	0.0011195	6.18E-07	0.035905	8.87E-07
24	0.141666667	0.002201667	0.036133333	0.0011195	6.54E-07	0.037711	7.66E-07
25	0.141	0.002176667	0.0363	0.0014	5.85E-07	0.039442	1.44E-06
26	0.141333333	0.002003333	0.036366667	0.00156	5.85E-07	0.038158	1.16E-06
27	0.141333333	0.002003333	0.036366667	0.001638333	5.85E-07	0.037914	1.39E-06
28	0.141666667	0.00183	0.036433333	0.001876667	5.16E-07	0.03767	1.79E-06
29	0.141666667	0.002015833	0.036283333	0.001498083	5.22E-07	0.038919	1.21E-06
30	0.141666667	0.002015833	0.036283333	0.001498083	5.22E-07	0.038919	1.06E-06
31	0.144	0.00183	0.034866667	0.002273333	5.22E-07	0.040169	1.01E-06
32	0.1255	0.001773333	0.0366	0.002155	5.28E-07	0.040084	9.36E-07
33	0.1255	0.001773333	0.0366	0.002155	5.13E-07	0.040084	1.01E-06
34	0.109333333	0.001716667	0.036766667	0.002433333	5.13E-07	0.039999	1.94E-06
35	0.128	0.001953333	0.037866667	0.00258	5.13E-07	0.040786	9.86E-07
36	0.128	0.001953333	0.037866667	0.00258	4.98E-07	0.040786	1.19E-06
37	0.146666667	0.00219	0.038966667	0.002726667	4.98E-07	0.041572	1.39E-06
38	0.148666667	0.00217	0.03955	0.002773333	4.98E-07	0.041009	1.04E-06
39	0.148666667	0.00217	0.03955	0.002773333	4.98E-07	0.041009	1.24E-06
40	0.150666667	0.00215	0.040133333	0.00282	4.98E-07	0.040446	1.19E-06
41	0.1505	0.002245	0.039316667	0.002903333	5.43E-07	0.039481	1.56E-06
42	0.1505	0.002245	0.039316667	0.002903333	5.43E-07	0.039481	1.16E-06
43	0.150333333	0.00234	0.0385	0.002986667	5.43E-07	0.038517	1.04E-06
44	0.150333333	0.002355	0.034083333	0.00312	5.88E-07	0.032766	8.85E-07
45	0.150333333	0.002355	0.034083333	0.00312	9.44E-07	0.032766	1.14E-06

Concentrations in mole/l Grey areas indicate average values (not analysed)

	[Na]	[K]	[Ca]	[SO4]	[SiO2]	[OH]	[Al]
NASK	0.14	0.002046	0.01995	0.003954		0	1.58E-06

Leaching step	[Na]	[K]	[Ca]	[SO4]	[SiO2]	[OH]	[Al]
46	0.150333333	0.00237	0.029666667	0.003253333	9.44E-07	0.027015	2.14E-06
47	0.148666667	0.002386667	0.028433333	0.003386667	9.44E-07	0.024499	2.01E-06
48	0.148666667	0.002386667	0.028433333	0.003386667	1.30E-06	0.024499	1.61E-06
49	0.147	0.002403333	0.0272	0.00352	1.58E-06	0.021983	1.66E-06
50	0.144666667	0.002596667	0.024266667	0.0036	1.58E-06	0.018711	2.51E-06
51	0.146	0.00263	0.024833333	0.00362	1.58E-06	0.019636	1.95E-06
52	0.147666667	0.00254	0.026966667	0.003656667	1.85E-06	0.017825	1.53E-06
53	0.149666667	0.002596667	0.027166667	0.00374	2.16E-06	0.016725	1.32E-06
54	0.149666667	0.002513333	0.0245	0.00384	2.16E-06	0.01642	1.29E-06
55	0.151	0.002516667	0.024166667	0.003953333	2.16E-06	0.015488	1.29E-06
56	0.145833333	0.0025	0.025733333	0.00356	2.46E-06	0.014541	1.23E-06
57	0.145833333	0.0025	0.025733333	0.00356	2.85E-06	0.01471	2.01E-06
58	0.161666667	0.001496667	0.0262	0.003655	2.85E-06	0.015054	1.97E-06
59	0.162	0.00158	0.025366667	0.003658333	2.85E-06	0.014591	2.35E-06
60	0.1174	0.000859333	0.020266667	0.003801667	3.25E-06	0.014145	2.47E-06
61	0.161666667	0.00147	0.0251	0.00383	3.74E-06	0.013299	6.77E-07
62	0.168333333	0.001586667	0.026133333	0.00387	3.74E-06	0.012791	1.77E-06
63	0.163333333	0.00147	0.026166667	0.004033333	3.74E-06	0.012647	1.44E-06
64	0.163	0.00152	0.024933333	0.00394	4.24E-06	0.012299	1.82E-06
65	0.157	0.001072333	0.023	0.00366	4.52E-06	0.011456	1.92E-06
66	0.164	0.001466667	0.023966667	0.00393	4.52E-06	0.011194	2.18E-06
67	0.141333333	0.00153	0.0221	0.004553333	4.52E-06	0.01103	1.39E-06
68	0.147	0.00218	0.014823333	0.0048	4.8E-06	0.010902	1.25E-06
69	0.149333333	0.002123333	0.024766667	0.004253333	5.13E-06	0.010067	1.32E-06
70	0.153666667	0.002363333	0.026866667	0.004193333	5.13E-06	0.009835	1.37E-06
71	0.15	0.00247	0.026233333	0.00375	5.13E-06	0.00939	9.1E-06
72	0.144666667	0.00192	0.037733333	0.0039	5.46E-06	0.009931	1.18E-06
73	0.1025	0.00188	0.0341	0.003933333	5.62E-06	0.009535	9.39E-07
74	0.146	0.002026667	0.031966667	0.003933333	5.68E-06	0.009023	1.73E-06
75	0.146333333	0.002036667	0.028566667	0.0039	5.86E-06	0.008101	6.77E-07
76	0.146333333	0.001993333	0.028366667	0.003666667	6.21E-06	0.00816	1.11E-06
77	0.168333333	0.002803333	0.0356	0.004766667	6.79E-06	0.008171	5.88E-06
78	0.1183	0.002803333	0.036966667	0.004066667	6.73E-06	0.007474	1.27E-06
79	0.166933	0.0024	0.0039233	0.005733333	6.52E-06	0.007216	1.06E-06
80	0.1755	0.002633	0.033266	0.004966667	6.5E-06	0.007383	1.3E-06
81	0.1473	0.0022666	0.026333	0.004233333	6.92E-06	0.007397	8.91E-07
82	0.15735	0.00205	0.0277	0.002866667	7.79E-06	0.007697	1.61E-06
83	0.15375	0.00205	0.02655	0.0027	7.61E-06	0.007157	1.61E-06
84	0.15455	0.00225	0.0274	0.003166667	7.45E-06	0.007687	1.3E-06
85	0.1565	0.00225	0.02725	0.0034	7.72E-06	0.007269	1.72E-06
86	0.161	0.00215	0.02705	0.003633333	7.62E-06	0.00731	1.09E-06
87	0.16325	0.00235	0.0237	0.0033	7.85E-06	0.006874	1.02E-06
88	0.15815	0.00245	0.02645	0.003633333	8.08E-06	0.006956	1.09E-06
89	0.1545	0.00235	0.02435	0.0037	8.5E-06	0.00679	1.07E-06
90	0.17625	0.00305	0.02475	0.004	8.66E-06	0.006694	1.55E-06
91	0.16925	0.00285	0.0265	0.0036	7.94E-06	0.00666	1.16E-06
92	0.1515	0.0035	0.0255	0.003833333	8.17E-06	0.006737	1.86E-06
93	0.1357	0.00305	0.0213	0.003633333	8.66E-06	0.0062	1.36E-06
94	0.15815	0.0022	0.0265	0.002933333	8.52E-06	0.004616	1.43E-06
95	0.1637	0.0026	0.0258	0.003133333	8.94E-06	0.00608	9.76E-08

Concentrations in mole/l			Grey areas indicate average values (not analysed)				
NASK	0.14	0.002046	0.01995	0.003954	0	1.58E-06	
Leaching step	[Na]	[K]	[Ca]	[SO4]	[SiO2]	[OH]	[Al]
96	0.1558	0.0027	0.0302	0.002766667	8.38E-06	0.006232	1.21E-06
97	0.1558	0.00285	0.0285	0.0027	9.15E-06	0.006139	1.57E-06
98	0.1479	0.0027	0.03065	0.0017	9.3E-06	0.006	1.4E-06
99	0.1494	0.00265	0.03025	0.0018	9.63E-06	0.005794	1.69E-06
100	0.14625	0.00255	0.02925	0.0017	9.59E-06	0.005799	9.69E-07
101	1.54E-01	0.0024	0.02915	0.0005	9.17E-06	0.006028	1.31E-06
102	1.52E-01	0.0024	0.029225	0.001	9.41E-06	0.005823	1.26E-06
103	1.51E-01	0.0024	0.0293	0.0015	9.65E-06	0.005617	1.21E-06
104	1.45E-01	0.00235	0.028225	0.000883333	9.68E-06	0.005534	1.44E-06
105	1.40E-01	0.0023	0.02715	0.000266667	9.72E-06	0.00545	1.67E-06
106	1.44E-01	0.002425	0.027275	0.000366667	9.97E-06	0.005437	1.49E-06
107	1.48E-01	0.00255	0.0274	0.000466667	1.02E-05	0.005424	1.31E-06
108	1.55E-01	0.00245	0.028525	0.000916667	1.08E-05	0.00542	
109	1.62E-01	0.00235	0.02965	0.001366667	1.08E-05	0.005416	
110	1.60E-01	0.002325	0.03285	0.001483333	1.08E-05	0.005293	
111	1.58E-01	0.0023	0.03605	0.0016	1.08E-05	0.00517	
112	1.50E-01	0.00255	0.0317	0.001116667	1.08E-05	0.00525	
113	1.42E-01	0.0028	0.02735	0.000633333	1.14E-05	0.005329	
114	1.48E-01	0.0027	0.0282	0.000933333	1.14E-05	0.005186	
115	1.55E-01	0.0026	0.02905	0.001233333	1.14E-05	0.005042	
116	1.56E-01	0.002725	0.0291	0.001966667	1.17E-05	0.005087	
117	1.56E-01	0.00285	0.02915	0.0027	1.20E-05	0.005133	
118	1.52E-01	0.00275	0.028125	0.002966667	1.17E-05	0.005277	
119	1.48E-01	0.00265	0.0271	0.003233333	1.14E-05	0.005421	
120	1.51E-01	0.00275	0.02815	0.001933333	1.08E-05	0.005483	
121	1.54E-01	0.00285	0.0292	0.000633333	1.03E-05	0.005544	
122	1.53E-01	0.002875	0.028825	0.0005	1.06E-05	0.005526	
123	1.52E-01	0.0029	0.02845	0.000366667	1.1E-05	0.005507	
124	1.50E-01	0.00275	0.0273	0.000866667	1.06E-05	0.005275	
125	1.48E-01	0.0026	0.02615	0.001366667	1.02E-05	0.005042	
126	1.43E-01	0.002425	0.025925	0.001383333	1.04E-05	0.004854	
127	1.38E-01	0.00225	0.0257	0.0014	1.07E-05	0.004665	
128	1.40E-01	0.002225	0.027425	0.001	1.13E-05	0.004814	
129	1.41E-01	0.0022	0.02915	0.0006	1.2E-05	0.004962	
130	1.43E-01	0.0025	0.029875	0.000983333	1.23E-05	0.004743	
131	1.45E-01	0.0028	0.0306	0.001366667	1.27E-05	0.004524	
132	1.47E-01	0.0027	0.028975	0.001966667	1.16E-05	0.004562	
133	1.49E-01	0.0026	0.02735	0.002566667	1.04E-05	0.0046	
134	1.44E-01	0.0028	0.026825	0.0023	1.09E-05	0.0045	
135	1.38E-01	0.003	0.0263	0.002033333	1.14E-05	0.0044	
136	0.1388	0.0015	0.02859	0.0056		0.004718	
137	0.1469	0.0022	0.02941	0.00415		0.005036	
138	0.1434	0.0021	0.03007	0.00575		0.004904	
139	0.1452	0.0019	0.03075	0.0043		0.004772	
140							
141	0.1485	0.00235	0.02998	0.00575			
142							
143	0.1336	0.00235	0.0285	0.00055			
144							
145	0.1497	0.00205	0.0364	0.00575			

Concentrations in mole/l			Grey areas indicate average values (not analysed)				
NASK	0.14	0.002046	0.01995	0.003954	0	1.58E-06	
Leaching step	[Na]	[K]	[Ca]	[SO4]	[SiO2]	[OH]	[Al]
146							
147	0.1417	0.0023	0.037	0.00575			

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TR 96-01

Bacteria, colloids and organic carbon in groundwater at the Bangombé site in the Oklo area

Karsten Pedersen (editor)
Department of General and Marine Microbiology,
The Lundberg Institute, Göteborg University,
Göteborg, Sweden
February 1996

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Microbial analysis of the buffer/container experiment at AECL´s Underground Research Laboratory

S Stroes-Gascoyne[1], K Pedersen[2], S Daumas[3],
C J Hamon[1], S A Haveman[1], T L Delaney[1],
S Ekendahl[2], N Jahromi[2], J Arlinger[2], L Hallbeck[2],
K Dekeyser[3]
[1] AECL, Whiteshell Laboratories, Pinawa, Manitoba,
 Canada
[2] University of Göteborg, Department of General
 and Marine Microbiology, Göteborg, Sweden
[3] Guigues Recherche Appliquée en Microbiologie
 (GRAM), Aix-en-Provence, France
1996

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Reduction of Tc (VII) and Np (V) in solution by ferrous iron. A laboratory study of homogeneous and heterogeneous redox processes

Daqing Cui, Trygve E Eriksen
Department of Chemistry, Nuclear Chemistry,
Royal Institute of Technology, Stockholm, Sweden
March 1996

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Revisiting Poços de Caldas. Application of the co-precipitation approach to establish realistic solubility limits for performance assessment

Jordi Bruno, Lara Duro, Salvador Jordana,
Esther Cera
QuantiSci, Barcelona, Spain
February 1996

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April 1996

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Criticality in a high level waste repository. A review of some important factors and an assessment of the lessons that can be learned from the Oklo reactors

Virginia M Oversby
VMO Konsult
June 1996

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A reappraisal of some Cigar Lake issues of importance to performance assessment

John Smellie[1], Fred Karlsson[2]
[1] Conterra AB
[2] SKB
July 1996