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Review of the Potential Effects of Alkaline Plume Migration from a Cementitious Repository for Radioactive Waste

Implications for Performance
Assessment

QuantiSci Ltd.

R&D Technical Report P60

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Review of the Potential Effects of Alkaline Plume Migration from a Cementitious Repository for Radioactive Waste

Implications for Performance Assessment

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Statement of use
This report reviews national and international R&D on processes relevant to effects of cementitious repositories on the host geology. This information will be useful to Agency staff involved in authorisations for disposal of radioactive waste.

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FOREWORD

The work reported here is the result of a project funded jointly by the UK Environment Agency, the Swiss National Cooperative for the disposal of radioactive waste (Nagra) and the Japanese Power Reactor and Nuclear Fuel Development Corporation (PNC). Overall management of the project was carried out by Dr Susan Duerden of the Environment Agency, and for Nagra by Dr Ingeborg Hagenlocher, and for PNC by Mr Kaname Miyahara (assisted at European management meetings by Mr Masao Shiotsuki). These individuals and their respective organisations are thanked for their support, help with producing text, and cooperation throughout the project.

Individuals from other organisations also made significant contributions to the project and are thanked for their help. Mr Tamotsu Chiba (Japanese Gas Corporation) wrote text describing his organisation's interests in alkaline plume migration. Mr Fred Karlsson of SKB (Swedish Nuclear Fuel and Waste Management Company) supplied reports and wrote text describing SKB's activities on the topic of alkaline plume migration. Dr Ian Crossland of UK Nirex Ltd. supplied a number of unpublished reports for consideration in a review of literature and Mr Leslie Knight of UK Nirex Ltd. made comments on a draft of the text. Dr Colin Hughes furnished text describing activities at the University of Manchester. Reviews by Carol Bruton (Lawrence Livermore National Laboratory, USA), Ian McKinley (Nagra), and Russell Alexander (Nagra/University of Bern) improved the manuscript substantially.

Other individuals acted as unofficial 'national contacts' to help identify organisations carrying out relevant research. These included: Jordi Bruno (Spain); Carol Bruton (USA), Jean-Claude Petit (France); and Pierre Toulhoat (France). These individuals are also thanked for their help.

Mrs Debbie Miller carried out a number of literature searches and Mr Paul Weston produced the diagrams. Mrs Hilary Moore produced copies of the report for publication.

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EXECUTIVE SUMMARY

Extensive use of cement and concrete is envisaged in the construction of geological repositories for low and intermediate-level radioactive wastes, both for structural, and encapsulation and backfilling purposes. Saturation of these materials with groundwater may occur in the post-closure period of disposal, producing a hyperalkaline pore fluid with a pH in the range 10-13.5. These pore fluids have the potential to migrate from the repository according to local groundwater flow conditions and react chemically with the host rock. These chemical reactions may affect the rock's capacity to retard the migration of radionuclides released from the repository after the degradation of the waste packages. The effects of these chemical reactions on the behaviour of the repository rock as a barrier to waste migration need to be investigated for the purposes of assessing the safety of the repository design (so-called 'safety assessment' or 'performance assessment').

The objectives of the work reported here were to: identify those processes influencing radionuclide mobility in the geosphere which could be affected by plume migration; review literature relevant to alkali-rock reaction; contact organisations carrying out relevant research and summarise their current and future activities; and make recommendations how the effects of plume migration can be incorporated into models of repository performance assessment.

The following paragraphs summarise the principal results and conclusions of the project.

A number of key processes affecting radionuclide migration has been identified which will be perturbed by the migration of a hyperalkaline pore fluid plume. These are: porosity and permeability properties; precipitation and co-precipitation behaviour; sorption; matrix diffusion; colloid stability and mobility; the mobilisation of organics from the host rock; and the behaviour of bentonite seals.

A review of literature pertaining to alkali-rock reactions in the radioactive waste, cement/concrete, and oil industries, and elsewhere was conducted. This confirmed the existence of much relevant data concerning: alkali-rock reaction mechanisms and mineral alteration sequences; changes in porosity and permeability; sorption of radionuclides; matrix diffusion behaviour; the thermodynamics and kinetics of likely reactions; and the mobility of organics.

Countries with current and planned research activities on alkaline plume migration were identified to include: Japan; Sweden; Switzerland; and the UK. These countries have many common interests on the issue of plume migration due to similarities in planned repository design, waste characteristics and potential repository host rocks. Therefore there is considerable opportunity for shared funding of research projects.

With regard to research carried out thus far, there are major uncertainties for performance assessment still remaining for: the overall spatial scale of alkaline alteration; the effects of

'early' Na-K dominated cement pore fluids; speciation-solubility behaviour of radionuclides at pH fronts; the mechanism of sorption behaviour in rock-water systems at high pH; matrix diffusion; colloid abundances at pH fronts; and the behaviour of bentonite at high pH.

Recommendations for performance assessment are that geosphere sub-models are produced for PA with variations of the above processes/properties to scope the potential effects upon radionuclide migration with regard to a reference case which assumes little or no perturbation of the far-field due to alkaline plume migration. Better definition of the scale of alteration is dependent upon the acquisition of better analogue data for repository scenarios and the use of more realistic models for chemical reaction and transport.

Key words radioactive waste; geological disposal; repository performance assessment; radionuclide migration; cement/concrete; alkali-rock reaction; radionuclide sorption behaviour; rock matrix diffusion; colloids; organics

1. INTRODUCTION

Cement is the preferred option for the encapsulation and back-filling of low and intermediate-level radioactive wastes in many countries' geological disposal programmes. As well as providing structural containment in some instances, cement provides a hyperalkaline environment which lowers metal corrosion and solubility. The relatively low solubility of cement and slow groundwater flow rates combine to promote long-lived hyperalkaline conditions in the repository environment. Laboratory and modelling studies (*e.g.* Atkinson, 1985; Atkinson *et al.*, 1987; Berner, 1992) suggest that depending upon groundwater flow rate and composition, pore fluids will be dominated by readily leachable potassium and sodium hydroxides for at least 1000 years after repository closure (so-called 'early' or 'young' leachates with pH = 13.5), which will be succeeded by calcium-dominated leachates (so-called 'evolved' or 'late' pore fluids). These evolved pore fluids have a pH of 12.5 (buffered by portlandite solubility), decreasing to pH 10-11 (buffered by CSH gel) perhaps for a time period up to 10^5 years after repository closure.

Hyperalkaline cement pore fluids will migrate with groundwater flow and move through the surrounding repository rock. The enhanced solubility and rate of reaction of most silicate minerals at elevated pH mean that movement of this 'alkaline plume' will be accompanied by chemical reaction of the host rock. For PA (performance assessment) it is necessary to assess how the barrier role of the far-field may be affected by these chemical reactions.

The evaluation of these effects is the subject of much interest for waste disposal authorities and regulators. This report attempts to summarise the state of knowledge worldwide on this subject and make recommendations for future activities with regard to performance assessment. In detail, this report presents:

- a list of key processes for performance assessment which may be affected by the hyperalkaline plume;

- a critical review of published and unpublished literature describing alkali-rock reactions both from the radioactive waste literature and elsewhere;

- a definition of remaining uncertainties;

- a description of current and planned future research activities in this area;

- suggestions for the incorporation of the effects of the hyperalkaline plume into PA.

The report does not consider site- or country-specific details of how local geological conditions may be impacted by the plume.

2. KEY PROCESSES INFLUENCING RADIONUCLIDE MIGRATION WHICH MAY BE AFFECTED BY THE ALKALINE PLUME

The following processes and properties influencing radionuclide migration have been identified as the most likely to be affected by migration of an alkaline plume:

- porosity and permeability;

- precipitation and co-precipitation;

- sorption (including ion exchange);

- matrix diffusion;

- colloids (their formation, stability, mobility, and interaction with radionuclides);

- mobilisation of natural organics;

- cement-bentonite seals.

Brief comments concerning how each of the above processes may be affected by migration of the alkaline plume are presented below.

2.1 Porosity and permeability of groundwater flowpaths

The porosity of groundwater flowpaths will change as a consequence of plume migration due to mineral dissolution and precipitation reactions. Changes in permeability are likely to accompany any change in porosity. Changes in porosity and permeability will vary in time and space around the waste repository. Widening of rock fractures due to mineral dissolution may be simultaneously accompanied by porosity decreases in the surrounding rock matrix due to diffusion and mixing of different pore fluids in the rock. Mineral precipitation may occur as a result of destabilisation of primary minerals in the rock and consequent replacement by thermodynamically more stable minerals, or by the mixing of cement pore fluids with ambient groundwater in the rock. The sealing of the rock matrix or fractures may lead to the diversion and focusing of groundwater/gas flow in certain directions. Spatial heterogeneity in the rock mass will cause chemical reaction and flow to produce channelling or fingering effects. The sealing of rock porosity may hinder the release of gas from the repository (due to metal corrosion and organic breakdown reactions), or lead to 'pulsing' of gas release as fractures close and re-open due to pressure build-ups. Mineral dissolution and precipitation reactions will be relatively slow so that a kinetic description of such processes may be necessary to

predict the detail of mineral parageneses and porosity-permeability changes over short time (10-100 years) and distance scales (of the order of 1-10 m). For greater distances and timescales, an assumption of chemical steady-state may be more appropriate to define the spatial scale of alteration.

2.2 Precipitation and co-precipitation

The precipitation of new solids/minerals will accompany plume migration throughout its lifetime/length due to the migration of sharp reaction fronts separating fluids of contrasting chemical composition. After degradation of the engineered containment (canisters, backfill), radionuclides released from the waste may migrate in advance of, together with, and/or after, the alkaline pore fluid plume. Some of these radionuclides will be incorporated into neoformed solids according to ionic charge, ionic radius and the structure of the solids concerned, thus retarding their migration. However, as the pattern of alteration solids evolves, solids incorporating radionuclides formed along the groundwater flow path may re-dissolve, to be replaced by solids more stable in the evolving pore fluid composition. These neoformed solids/minerals may not reincorporate the radionuclides released to solution by the preexisting solid/mineral.

2.3 Sorption

The sorption and ion exchange properties of the far-field will evolve with time and distance in accordance with the changes in its mineralogical and chemical properties due to alkaline plume migration. Aqueous speciation will vary according to the changing distribution of different pore fluid compositions along groundwater flowpaths. Sorption and ion exchange will thus be affected by changes in aqueous speciation as pore fluid compositions evolve as well as changes in the nature of the solid substrate. There will be a tendency for the de-stabilisation of well-crystalline, anhydrous/poorly hydrated minerals such as silica polymorphs, feldspars, micas, carbonates and oxides, to be replaced by poorly crystalline, more hydrous alkali/alkaline-earth zeolites, calcium silicate hydrates and hydroxides. These transformations will change the capacity of the far-field to retard radionuclide migration. Ion exchange sites on clays in particular will be saturated with the major cations of the ambient pore fluid, being Na and K during initial stages of cement evolution, and Ca during later stages, but exchange of radionuclides for these elements may still take place if the energetics of the reaction are favourable.

2.4 Matrix diffusion

The matrix diffusion properties of the far-field may be affected by plume migration. Fracture surfaces may be sealed by neoformed solids, thus preventing radionuclide diffusion into the

rock matrix, or porosity in the rock matrix may be increased or decreased according to the mineral transformation reactions concerned. Zones of porosity increase and decrease may occur simultaneously at different distances into the rock matrix.

2.5 Colloids

The abundance and stability of colloids in far-field groundwaters will be affected by plume migration. Inorganic and organic colloids naturally present in the groundwater may be de-stabilised (dissolved and/or flocculated) in hyperalkaline pore fluids, leading to a reduction in colloid abundances. Alternatively, colloids could be created at pH fronts, where contrasts in solubility (particularly for polymorphs of silica) occur.

2.6 Mobilisation of natural organics

Naturally-occurring solid organic materials in the rock matrix may be liberated for complexation with radionuclides by dissolution of the rock matrix as a consequence of plume migration. This process is probably only relevant to sedimentary rock types which may contain amounts of organic material dispersed in the rock matrix.

2.7 Cement-bentonite seals

Some disposal concepts employ bentonite in conjunction with cement to enhance repository integrity. Bentonite contacted by cement pore fluids may undergo dissolution-precipitation reactions leading to partial conversion of the clay to zeolites and silica. This will decrease the plasticity and porosity of the bentonite. Additionally, ion exchange of Na^+ ions on clay surfaces by Ca^{2+} from 'evolved' cement pore fluids will reduce the swelling capacity of the bentonite.

3. LITERATURE REVIEW

The review is presented in the following categories:

- radioactive waste;

  - mineralogical investigations and experimental studies

  - modelling

  - natural systems (analogues)

  - reviews

- cement-aggregate reactions;

- hydrocarbon reservoir remediation;

- others.

A summary of experimental studies carried out under each of the above topics is presented in Appendix I.

3.1 Radioactive waste

3.1.1 Mineralogical investigations and experimental studies

These studies have been conducted to provide one or more of the following types of information:

- mechanisms of reaction of minerals and rocks with cement pore fluids. In general, these studies have been carried out at temperatures in excess of those expected in waste repositories in the interests of accelerating reactions;

- estimates of the rates of reaction of single minerals and their dependence upon pH for incorporation into quantitative modelling studies;

- tests of models of chemical reaction and fluid flow;

- estimates of sorption coefficients of metal ions on calcium silicate hydrates and zeolites.

The BGS (British Geological Survey) has investigated the reaction of a number of minerals and rocks with calcium hydroxide, NaOH/NaCl buffer solutions, mixed Na-K-Ca hydroxide fluids and so-called 'young near-field pore water' and 'evolved near-field pore water' (Savage et al., 1991, 1992a, 1992b; Rochelle et al., 1992, 1994a, 1994c, 1995b). Batch experiments were conducted at 70 °C and involved disaggregated pure samples of quartz, albite, K-feldspar, muscovite, biotite, Ca-smectite, kaolinite, chlorite, calcite, dolomite, and lithologies of the Borrowdale Volcanic Group (disaggregated samples and disks of bulk rock, and disaggregated samples of carbonate, and high-temperature silicate fracture fillings).

In general, these studies revealed rapid loss of Ca from all fluids and the production of a variety of CSH and CASH gels/solids as surface layers on starting materials. Ettringite was a product in experiments involving fluids with appreciable sulphate contents (simulated Sellafield near-field groundwaters). The Ca-smectite experiment showed evidence of Ca-Na-K ion exchange between fluid and clay. Hydrogarnets and zeolites were tentatively identified as products with feldspars and sheet silicates. The formation of alteration layers did not inhibit further dissolution of the primary mineral grains. Greater reactivity of the starting materials in the mixed alkali hydroxide fluids was noted, although the solid products were almost as great as those observed in the $Ca(OH)_2$ fluids. Although porosity changes were not measured directly, cementing of mineral grains was noted for both fluids. The following reaction sequence was observed: dolomite > calcite > quartz > microcline > albite > chlorite > muscovite. Quartz and albite had dissolution rates which increased with increasing pH (Table 3.1). Fluids in experiments with quartz reacted with Na-K-Ca-OH showed dramatic increases in silica after removal of Ca (Figure 3.1). The presence of dolomite in BVG lithologies had a large effect in lowering the pH of ambient fluids (from 11.5 to 10) by the precipitation of calcite and brucite. Zeolites and feldspars were inferred from modelling studies to be stable during the experiments.

These studies have been extended to investigate the kinetics of reaction of single minerals in both mixed flow (Rochelle et al., 1994b, 1995a) and column experiments (Bateman et al., 1995). Rochelle et al. (1994b) studied the dissolution of chlorite (the principal ferromagnesian mineral in the BVG lithologies at Sellafield) at 25 and 70 °C and noted that although the rate of chlorite dissolution increased with increasing pH, its absolute rate was at least two orders of magnitude less than that of albite and four orders of magnitude less than that of quartz at 25 °C and pH 13. It is unlikely therefore that dissolution of chlorite will contribute significantly to the retardation of the alkaline plume.

Carbonates are unstable in hyperalkaline fluids, with calcite being replaced by portlandite, and dolomite by calcite and brucite (Poole and Sotiropoulos, 1980). Rochelle et al. (1994b) reviewed data available in the literature for the rate of dissolution of carbonate minerals (calcite, dolomite, aragonite, witherite, magnesite, strontianite, siderite). In general, the dissolution rates for these minerals decrease with increasing pH in the alkaline regime (pH > 7), but data for pH > 10 are lacking. At pH = 10, the following order of dissolution rate was noted: calcite, aragonite, witherite > dolomite > magnesite.

Table 3.1   Rate constants of mineral dissolution obtained in radioactive waste experimental studies.

mineral	log rate§ mol m^{-2} s^{-1} (extrap- olated to pH 0)	exponent of H+ activity¶	T °C	pH at experi- mental T	experimen- tal system	author
quartz	-19.42	-1.0*	70	11.4 & 12.0	batch/flow	Savage et al. (1991, 1992b)
albite	-25.48	-1.4*	70	11.4 & 12.0	batch/flow	Savage et al. (1991, 1992b)
chlorite	-15.0	-0.3	25	7.7, 9.9, 12.5	mixed flow	Rochelle et al. (1994b, 1995a)
chlorite	-19.9	-0.7	70	6.7, 10.2, 11.6	mixed flow	Rochelle et al. (1994b, 1995a)

§ rate is calculated from release of Si to solution, and assumes stoichiometric dissolution. ¶ assumes a rate law where rate = k $[a_{H+}]^n$. * these figures are based on two data points only and conflict with data for the same experiments presented in Savage et al. (1992b), where n was assigned as -0.5. The latter interpretation was based on consistency of the data (within experimental error) with those reported by the more pH-extensive study of Knauss and Wolery (1986).
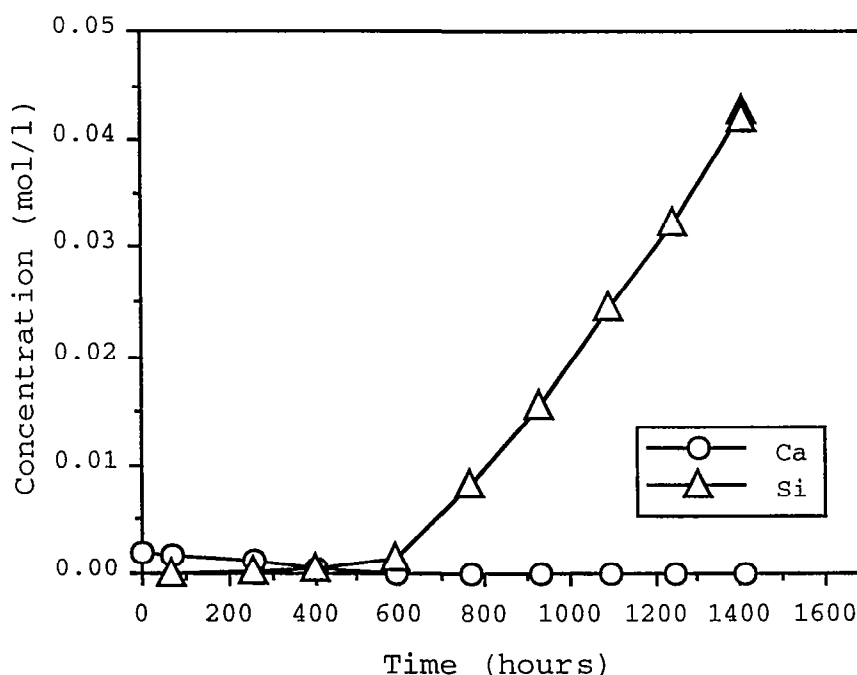

Figure 3.1   Concentration-time profile for the fluid in a batch quartz-mixed alkali experiment at 70 °C (from Savage et al., 1992b). Note the increase in Si concentration after removal of Ca from the fluid.

Bateman *et al.* (1995) carried out experiments with quartz, albite, calcite, and quartz + muscovite in individual columns at 70 °C with both mixed alkali and calcium hydroxide fluids in an attempt to supply data to test a coupled model of reaction and fluid flow ('PRECIP'). Solid products were portlandite [$Ca(OH)_2$] in the calcite columns, and a variety of compositions of CSH and CASH gels/minerals in the other columns. No zeolites were observed, although zeolite and K-feldspar were predicted to form in the muscovite column from the PRECIP modelling. $Ca(OH)_2$ fluids produced considerable amounts of solid products such that it was difficult to maintain a constant flow rate in the columns due to porosity blockages. Enough solid material was produced in the columns with mixed alkali hydroxide fluids that overall porosity decreases were noted in each of the columns, despite the effects of enhanced dissolution observed in the primary mineral grains. PRECIP simulations were similar to observed results although the distribution of alteration phases was much more limited spatially in the model simulations. This was attributed to overestimation of mineral reactive surface area and reaction rate (both dissolution and precipitation) in the simulations.

Braney *et al.* (1993) passed a solution of $Ca(OH)_2$ through a 10 cm column of sandstone at 25 °C and monitored changing composition of the eluate with time (Figure 3.2). Decreases in pH and Ca concentration were explained by a model involving the kinetic dissolution of quartz and the equilibrium precipitation of CSH phases. A period of sorption of Ca onto Fe-oxides was necessary to explain initial buffering of pH and Ca. SEM examination of the sandstone after the experiment revealed effects of quartz and feldspar dissolution and the precipitation of CSH gels.

Chermak (1992, 1993, 1996) has investigated the reaction of the Palfris and Opalinus Clays (two of the rocks under consideration in the Swiss radioactive waste disposal programme) with NaOH and KOH at 75, 150, 175 and 200 °C. Experiments at 75 °C were conducted in both batch and flow-through configurations. No calcium was present in the starting fluids. At 150, 175 and 200 °C, solid products were various zeolites, feldspar and sheet silicates, according to the alkali metal present. In the KOH solutions, phillipsite, K-feldspar and rectorite formed, whereas in NaOH, the products were analcime, vermiculite and Na-rectorite. These reactions produced a decrease in the ambient pH of the fluids (10.5 at 200 °C, 11.5 at 150 °C and 11.8 at 100 °C). In the flow-through experiments at 75 °C, tobermorite was seen as a precipitate in both shales. In the batch experiments at 75 °C, tobermorite formed after 20 days, and after removal of all calcite from the shales, the solid products were then albite in the NaOH experiments and K-feldspar and K-zeolites in the KOH experiments. In the starting materials at 75 °C, calcite, ankerite, siderite, quartz and kaolinite were all reactive.

Milodowski *et al.* (1994) reported mineralogical investigations of the products of (microcosm) experiments involving cement, groundwater, rock and canister metals at 25 °C at time periods up to 4.5 years. The rock was a 'marl' from Oberbauenstock, Switzerland. Alkali-rock reaction was manifested in terms of conversion of some of the marl to clays similar to saponite, corrensite or mixed layer chlorite-smectite. Quartz in the marl had reacted to produce a CSH gel.
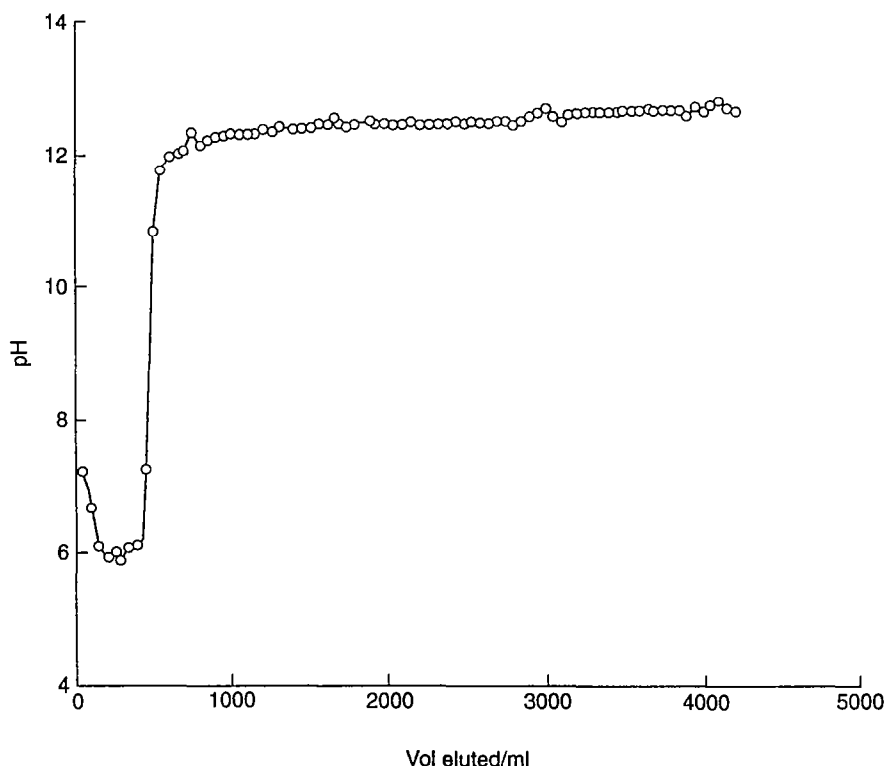
Figure 3.2 pH-time profile from an experiment passing saturated Ca(OH)$_2$ solution through a core of Clashach Sandstone (from Braney *et al.*, 1993). The initial low pH represents the flow of 4 pore volumes through the rock which was interpreted by exchange of Ca^{2+} from the fluid for H$^+$ ions sorbed on interstitial Fe-oxides in the sandstone. The slow increase of pH after ~700 ml eluted (after the rapid increase in pH at ~ 600 ml eluted) represents consumption of H$^+$ due to the slow dissolution of quartz and aluminosilicates in the core.

Komarneni *et al.* (1988) noted surface exchange of Pb, Cd, Mn, Zn and Cu for Ca in tobermorite. Ewart *et al.* (1990) report K$_d$ values of 60 m^3 kg^{-1} and 20 m^3 kg^{-1} for Am^{3+} and Pu^{4+} on CSH, respectively. Berry (1996) measured higher sorption coefficients for U and Pu and similar Kd's for Th for alkaline altered samples of Borrowdale Volcanic Group lithologies as compared with unaltered samples. Berry attributed this to the actinides forming negatively-charged aqueous complexes at high pH and CSH minerals being strong sorbents at high pH due to their high zero point of charge and thus retaining a significant quantity of positive charge.

Hoyle and Grutzeck (1989) carried out experiments to characterise the uptake of caesium during

the curing of cement. They noted that the uptake of caesium was directly related to the composition of the cement and increased with increasing Al and Si content. Pollucite (the Cs analogue of analcime) and other zeolites were identified as being the Cs hosts.

3.1.2 Modelling

Several modelling studies have been carried out in attempts to predict the scale and effects of the alkaline plume and also to interpret mineralogical parageneses at natural analogues.

Early studies of this type used closed system reaction-path models (no transport) to evaluate potential mineral parageneses and porosity changes. Fritz *et al.* (1988) simulated the reaction of granite, cement and water at 25, 60 and 100 °C. Cement pore fluids were approximated by saturated $Ca(OH)_2$ solutions. They concluded that minerals such as zeolites would form in the system, but that porosity changes would be positive (*i.e.* increase). Unfortunately, Fritz *et al.* did not include data for CSH solids in their calculations which limits the relevance of their conclusions. A subsequent study focused on bentonite-alkali reaction at 100 and 150 °C (Fritz and Madé, 1991). Again, data for CSH phases were missing from the calculations, but major amounts of bentonite dissolution were predicted, along with the precipitation of zeolites, calcite and kaolinite. Lundén and Andersson (1989) modelled the mixing of cement pore fluids with groundwater using PHREEQE and identified supersaturations (potential precipitates) of calcite, chlorite, hydroxyapatite and laumontite. Again, data for CSH solids were not included in these calculations. Savage and Rochelle (1993) modelled the reaction of a simplified granitic rock system with both Na-K-Ca hydroxide and calcium hydroxide fluids using EQ3/6 (version *3245.1090*; database R10). Mineral dissolution kinetics were included in the calculations. A temporal mineral alteration sequence of CSH solids, followed by zeolites and feldspar was predicted. Porosity increases for Na-K-Ca-OH fluid and decreases for the $Ca(OH)_2$ fluid were predicted, respectively. Uncertainties in the thermodynamic and kinetic data for zeolites and feldspars limited the definitive description of porosity and mineral paragenesis.

The effects of transport were first included in attempts to predict the interaction of cement with clay at shallow sites for the disposal of radioactive waste in the U.K. (Haworth *et al.*, 1988; Jefferies *et al.*, 1988). Haworth *et al.* (1988) used CHEQMATE to simulate advection, diffusion and dispersion and approximated the chemical system by calcite, clay and calcium hydroxide. The chemical reaction mechanism was considered to be ion exchange only, with no inclusion of dissolution-precipitation effects, or changes in porosity. A (conservative) migration distance for the plume of 5 m after 1000 years was calculated (assuming a pore water velocity of 10^{-10} m s^{-1}). This modelling work was reinforced by laboratory titration experiments with clay (Jefferies *et al.*, 1988). Through diffusion[1] of $Ca(OH)_2$ in clay

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[1] 'Through-diffusion' experiments use both high and low concentration reservoirs of the diffusing solute species on each side of the rock sample investigated so that diffusion coefficients are determined from solute breakthrough curves, whereas so-called 'in-diffusion' experiments, rely on one solute reservoir and diffusion is evaluated by analysis of thin sections of the rock sample after the experiments have been completed.

experiments conducted in parallel with the modelling produced a decrease in diffusivity of one order of magnitude (from 4×10^{-11} to 4×10^{-12} m^2 s^{-1}). A visible 'mineralogical front' was believed to have caused this decrease in diffusivity, but no characterisation of the mineralogy was conducted.

The so-called 'quasi-stationary steady-state' approach to water-rock interaction modelling has been applied to cement pore fluid migration by Lichtner and Eikenberg (1994). Lichtner and Eikenberg (1994) used the MPATH code to investigate the migration of cement pore fluids through a 'marl' at a hypothetical repository site in Switzerland. The modelling included mineral dissolution kinetics and aqueous speciation, but not the effects of changing porosity on the groundwater flow field, nor ion exchange. These authors emphasised that for long time spans mineral dissolution rate constants are unimportant in governing the rate of plume migration. The rate of plume migration was predicted to be 1-2 orders of magnitude less than that of the groundwater (the latter travelling at an assumed rate of 1 m/year). A sequence of CSH phases, clays, and zeolites was predicted to form from the interactions. A porosity increase (from 10 to 25 %) near the repository (on the order of centimetres to one metre) and a total loss of porosity a few metres beyond was predicted (Figure 3.3). The total distance of plume migration was calculated to be ~1000 m, although the omission of the effects of porosity change makes this conclusion questionable. Adding Na and K hydroxides to the simulated cement pore fluids made little difference to the conclusions concerning OH- migration and porosity changes. The precise detail of the results was sensitive to the mineral dissolution rates incorporated in the modelling, but not the precipitation rates of secondary minerals.

Haworth and Noy (1995) compared the use of the computer codes CHEQMATE and PRECIP to model cement pore fluid migration along a fracture in crystalline rock. CHEQMATE is a finite difference 1-D code incorporating the effects of advection, diffusion, mineral dissolution and precipitation and sorption. PRECIP is a finite-difference 1-D code incorporating the effects of advection, diffusion, dispersion and mineral dissolution-precipitation. CHEQMATE iterates between the flow and chemistry solver, whereas PRECIP is directly coupled. PRECIP can incorporate the effects of changing porosity on the fluid flow boundary conditions. An aqueous speciation model is included in CHEQMATE, but not in PRECIP. Both Na-K-Ca-OH and $Ca(OH)_2$ fluids were considered, along with mineral reaction kinetics. Groundwater compositions from deep boreholes at Sellafield were assumed to fill the hypothetical fracture. For the mixed alkali fluids, zeolites were the dominant products, whereas CSH phases dominated for the calcium hydroxide fluid. A porosity increase was predicted near the fluid inlet for the mixed alkali fluid (0.2 m from the inlet), whereas porosity reduction occurred beyond (Figure 3.4). For the $Ca(OH)_2$ fluid, porosity was reduced to zero within 0.2 m of the fluid inlet. PRECIP was also used to carry out calculations assuming a changing porosity field, using the cubic law relationship between porosity and permeability. For this scenario, flow ceased (due to filling of porosity) in a 20 μm wide fracture after 16 years of the simulation.
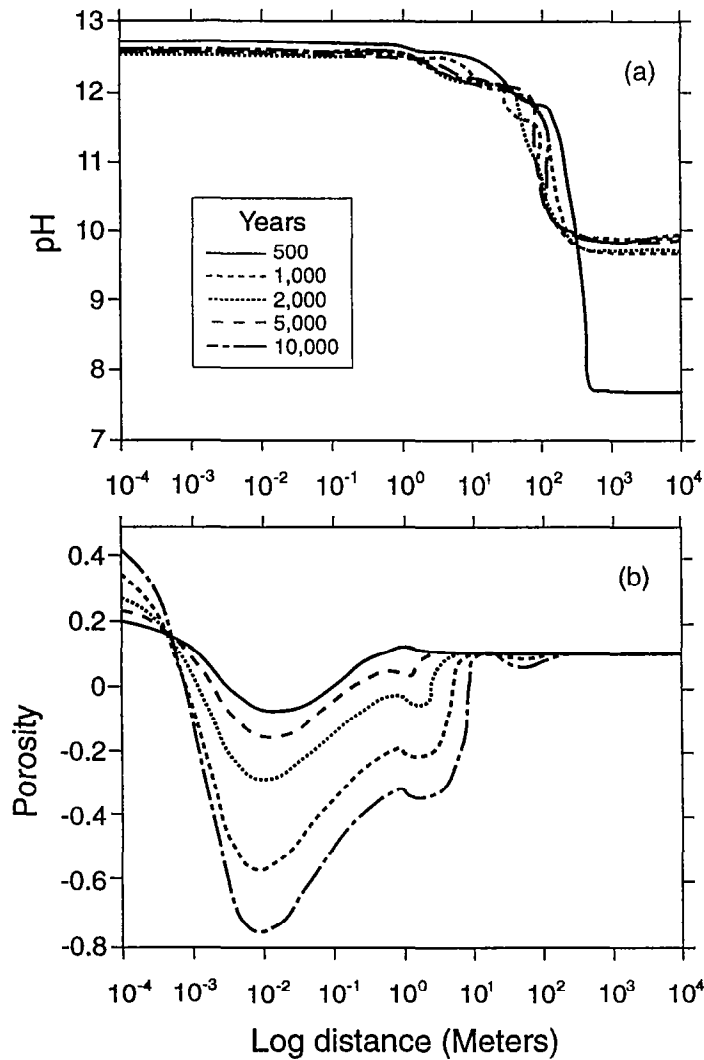
Figure 3.3 Calculated migration of a pH plume (mixed Na-K-Ca-OH) from a hypothetical waste repository in Valanginian Marl at Wellenberg in Switzerland (from Lichtner and Eikenberg, 1994). Note that the volume of minerals is expected to exceed that of porosity available in the rock after less than 500 years in the simulation. The extrapolation of the effects of the plume to distances of 1000 m is therefore probably unwarranted. Note also the increase in porosity close to the inlet (up to 1 cm from the inlet) and porosity decreases beyond this distance.
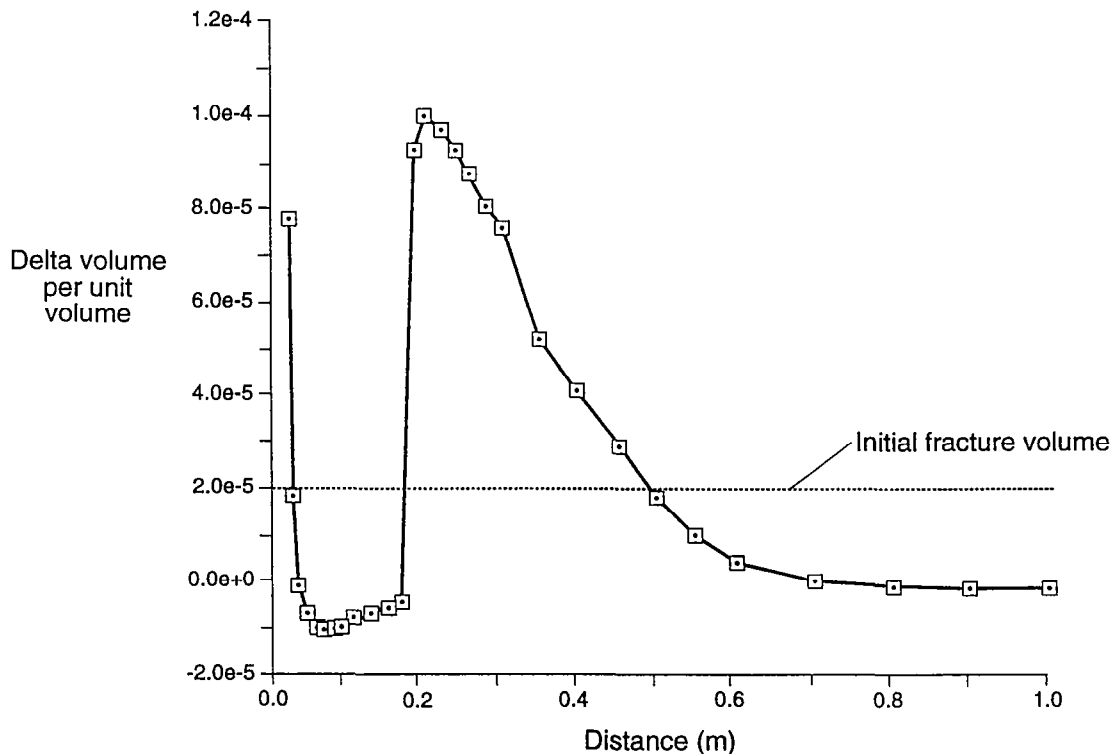
Figure 3.4 Changes in the volume of solids associated with the migration of a mixed Na-K-Ca-OH fluid through a 20 μm fracture in 'granitic rock' at a time of 300 years (from Haworth and Noy, 1995).

Steefel and Lichtner (1994) investigated reactions in an alkali-filled fracture adjacent to marl using the 1DREACT computer code. Simulation of diffusion of fluid into the rock matrix suggested that the rock matrix pores could be filled by calcite precipitation within 10-500 years (Figure 3.5). A slight increase in the porosity of the rock adjacent to the fracture was also calculated. A depth of 50 cms in the marl was required to neutralise the high pH plume over 30 years. The calculations were sensitive to the dissolution rates of primary, but not the precipitation rates of secondary, minerals. However, it should be noted that Steefel and Lichtner ignored nucleation kinetics and used identical rate constants for both dissolution and precipitation. Both these assumptions mean that precipitation kinetics may not be unimportant. Changing porosity conditions were included in the transport calculations.

Crompton *et al.* (in press) modelled the interaction of cement, clay, and rock (a mixture of montmorillonite, calcite and silica) in 2-D using the code ARASE. This study demonstrated the capability of current software and computer systems to be able to tackle complex chemical and spatially heterogeneous systems over reasonable timeframes. These authors emphasised the need to investigate such systems in two spatial dimensions and using fully coupled processes.
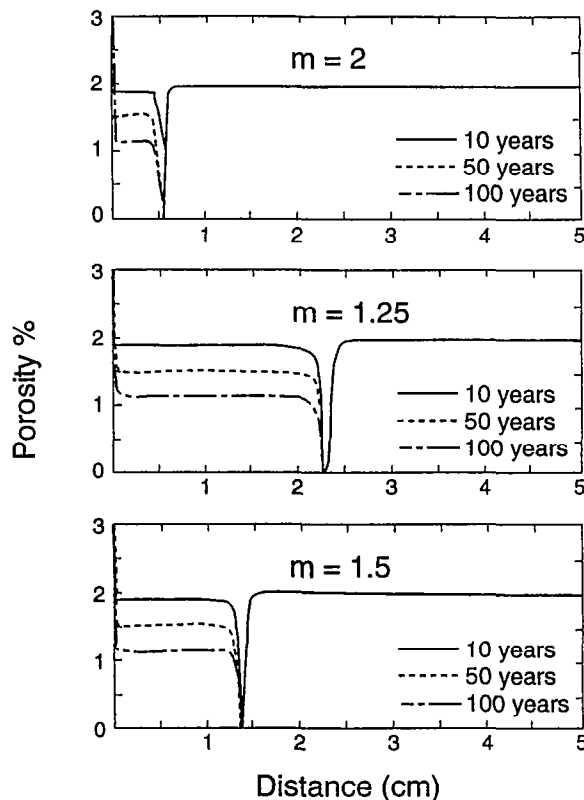
Figure 3.5 Predicted porosity evolution for the rock matrix adjacent to a fracture in marl filled with Na-K-Ca-OH fluid due to diffusion (and consequent dissolution-precipitation reactions) into the rock matrix (from Steefel and Lichtner, 1994). This example includes the incorporation of the effects of changing porosity on the diffusion calculations. 'm' is an exponent relating to the degree of cementation of the matrix.

Eikenberg (1990) investigated silica solubility at high pH. He noted that there is considerable uncertainty concerning the aqueous speciation of silica at high pH which leads to uncertainty in calculated solubilities of the silica polymorph minerals and aluminosilicates.

Thoenen (1996) has reviewed the formation of alteration minerals in hyperalkaline systems of relevance to radioactive waste (experiments, modelling and natural analogues), in an attempt to summarise the most likely minerals to form from a repository alkaline plume. He has also estimated thermodynamic data for zeolites in an attempt to produce a self-consistent database for these minerals. His review focuses on what he views as an apparent inconsistency between alteration minerals predicted by coupled modelling studies and those observed at the Maqarin natural analogue (see below for further details of Maqarin) and suggests that zeolites should be predicted to form from hyperalkaline pore fluids close to the repository. However, it is not clear to the present author that these perceived inconsistencies in observed and predicted mineral sequences at Maqarin really exist.

3.1.3 Natural systems (analogues)

The study of natural systems relevant to the migration of a hyperalkaline plume from a cementitious radioactive waste repository has focussed on Maqarin, Jordan. Here, the natural combustion of bituminous limestones has resulted in the occurrence of cement clinker-type minerals and their hydration products. Hyperalkaline spring waters of pH 12.5 occur in dam foundation investigation adits and valley sides. Opportunity exists for the collection and analysis of the spring waters, and their interaction not only with limestones, but also with chert and basalt colluvial materials.

The Maqarin analogue has been investigated since 1990, in three phases, focussing on issues such as: water-rock interaction; trace element solubility and model testing; microbiology; colloid occurrence and stability; organics; and clay stability. Data collection for Phase III was concluded in the autumn of 1996, with a view to the production of a final report in autumn 1997. Reviews of the background and conclusions of the studies carried out so far are provided by Alexander (1995), and Alexander and Mazurek (1995). There are numerous reports and papers providing extensive detailed coverage of the various aspects of the project as follows:

> *water-rock interaction* - Maqarin Natural Analogue Site Study Group (1991), Khoury *et al.* (1992), Milodowski *et al.* (1992), Milodowski (1994), Savage (1996), Alexander *et al.* (1996);
>
> *groundwater chemistry* - Clark *et al.* (1994);
>
> *colloids* - Pearce *et al.* (1996);
>
> *microbiology* - West *et al.* (1995);
>
> *database testing and trace element modelling* - Alexander *et al.* (1992), Linklater *et al.* (1994).

It is not intended to reproduce the conclusions of these publications here. Instead, attention will be placed upon the implications of the findings of the Maqarin analogue for some key issues related to understanding the migration of an alkaline plume from a waste repository.

Scale and extent of the alkaline plume. There are few quantitative conclusions which can be made from evidence at Maqarin. Differences in host rock lithological and hydrogeological characteristics between Maqarin and those expected in a waste repository make direct comparisons tenuous. Lithologies at Maqarin are dominated by limestone, whereas most repository host rocks are likely to have mineralogical compositions dominated by silicate and

aluminosilicate minerals[2]. Aluminosilicates and oxides provide much greater retardation capacity for the high pH plume than the (calcium) carbonates in the Maqarin limestones. Hydrogeological data for the Maqarin rocks are sparse. Porosities of 30 % (Milodowski, 1994) and permeabilities of 10^{-7} m s^{-1} (Alexander and Mazurek, 1995) in the Maqarin limestones are much greater than those in typical crystalline rock considered suitable for waste disposal (< 0.1 % and < 10^{-10} m s^{-1}, respectively - *e.g.* Nagra, 1994), although Alexander and Mazurek (1995) report macro and micro porosity of rock formations (principally fault gouges) at Wellenberg which range up to 10 % each. Ages of minerals range from ~10^4 a for tobermorites and zeolites present as products of water-rock interaction, whereas a diagenetic calcite provides an age of 10^5-10^6 a as a maximum age for the metamorphism which produced the cement zone minerals, indicating a long-lived period of hydration and alteration (Milodowski, 1994; Alexander and Mazurek, 1995). Groundwater isotopic information suggests groundwater ages older than 50 years so that no firm conclusions can be drawn concerning groundwater residence times and flowpaths. Differences in tectonic regimes between Maqarin and potential repositories also inhibit direct translation of data.

Alkali-rock reaction mechanisms. There is excellent detailed evidence for the reaction of a number of rock types (limestone, chert, basalt) with an essentially Ca-OH-SO$_4$ fluid of elevated pH at Maqarin (Milodowski *et al.,* 1992; Milodowski, 1994). Although inevitably these reactions are complex and highly variable, in general, a reaction sequence of the following can be observed where Ca-OH-SO$_4$ fluids initially contact limestones: carbonate, gypsum -> ettringite-thaumasite -> CSH gel -> zeolites (Milodowski, 1994; Alexander and Mazurek, 1995). The reverse of this alteration sequence can be observed where fluids have already reacted appreciably with the impure limestones. These sequences are interpretable by reaction of hyperalkaline fluids with rocks containing aluminosilicate minerals and by considering how much rock the fluids have previously reacted with (Savage, 1996) [Figure 3.6]. Although there are limitations in the varieties of minerals contained within thermodynamic databases employed in geochemical and coupled reaction and flow models, the essential features of these mineral parageneses can be understood from theoretical geochemical considerations and by numerical simulations (Savage, 1996). The reaction sequences observed at Maqarin are directly relevant to understanding the reaction of evolved (*i.e.* calcium-dominated) hyperalkaline fluids with rocks, albeit with the understanding that the Maqarin groundwaters have particularly high sulphate contents, and that Maqarin rock types are aluminosilicate-poor (with the exception of the basalt colluvium). Unfortunately, these mineral parageneses tell us very little about the reaction of Na-K dominated cement pore fluids with rocks. The most hyperalkaline springs at Maqarin, the so-called 'Western Springs' contain levels of Na and K which are an order of

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[2]However, it should be noted that the mineralogical composition of bituminous limestones at Maqarin lies within the range (albeit at the extreme end) of rock compositions at the potential Swiss site for L/ILW disposal, Wellenberg. Limestones at Maqarin have clay and calcite contents of approximately 8 and 75 %, respectively, whereas the Palfris Formation and Vitznau Mergel at Wellenberg have 2-60 and 10-90 % clay and calcite, respectively (Alexander and Mazurek, 1995). Similarly, ankerite and dolomite are present as fracture fills in the Borrowdale Volcanic Group at Sellafield, so that their behaviour may be comparable with the Maqarin limestones.

Groundwater flow →

Plume migration

REPOSITORY

pH, Ca

Al , Si

Concentration

Time / distance

CSH (high Ca/Si)
CSH (low Ca/Si)
CASH
low Si/Al zeolite
high Si/Al zeolite

Enhanced
porosity?
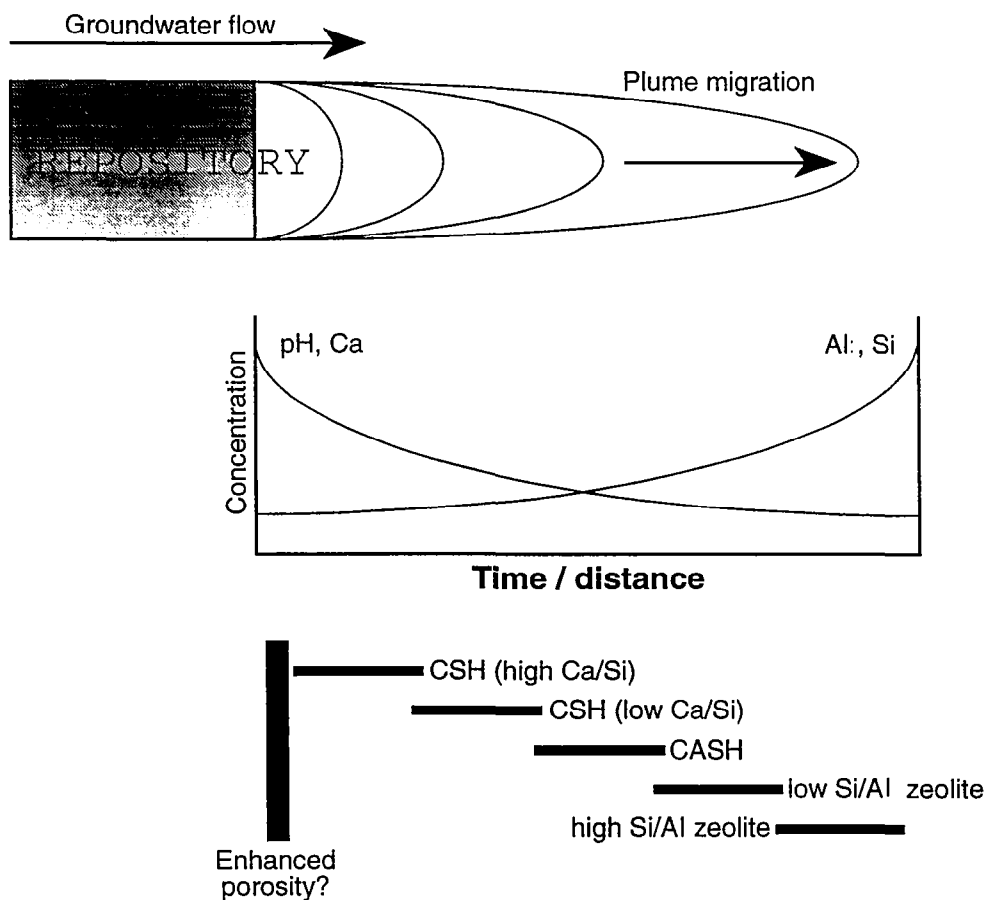
Figure 3.6 Mineral alteration sequence associated with the movement of an alkaline plume from a waste repository, by analogy with the mineral paragenetic sequences observed at Maqarin (from Savage, 1996).

magnitude less than those expected in 'early' cement pore fluids (Savage, 1996; Alexander and Mazurek, 1995).

Porosity-permeability changes. Evidence from Maqarin shows consistently that the interaction of calcium-dominated hyperalkaline fluids with limestones, chert and basalt decreases porosity (and probably permeability), ultimately sealing fractures where alteration is taking place (Milodowski *et al.*, 1992; Milodowski, 1994; Alexander and Mazurek, 1995). Age dating of one such fracture suggests that this occurs over 10-100 years (Alexander and Mazurek, 1995). However, reactivation of fractures through tectonic/erosional activity has maintained spring activity in the Maqarin system over a 10^5 year time period.

Matrix diffusion. Wall rock alteration takes place within 0.5 to 4 mm of fractures at Maqarin (Alexander and Mazurek, 1995). There is a zone of enhanced porosity immediately adjacent to

the fracture and precipitation of a zone of calcite approximately 1 mm into the rock. This suggests that the rock matrix is initially available to the diffusion of aqueous species from a fluid-filled fracture, but that this diffusion may be subsequently inhibited due to the filling of porosity in the matrix due to mineral precipitation.

Radionuclide retardation. There are no quantitative data available from Maqarin concerning radionuclide retardation, although evidence exists for the co-precipitation of U, Th, Se, Ni, Pb (up to 10's ppm) in zeolites, brucite, jennite and CSH gels (Milodowski, 1994).

Colloids. Colloid abundances in groundwaters at Maqarin are low, of the order 10^4 ml-1. Pearce *et al.* (1996). However, the samples taken for colloid analysis at Maqarin may not be the most appropriate to assess potential maxima of colloid abundances in hyperalkaline systems. This is because Si concentrations in Maqarin hyperalkaline groundwaters are buffered at low levels (< 1 mg/l) by ettringite-thaumasite solubility (Savage, 1996). High silica concentrations can develop in pore fluids at elevated pH in the absence of Ca (Savage, 1996). These fluids may produce very high concentrations of colloids at pH fronts where they mix with groundwaters of lower pH.

Organics. Humic acids are absent from Maqarin groundwaters, but organic material in the limestones appears to be dissolved during alkaline alteration and re-precipitated at zones of porosity reduction in the rock matrix (Alexander and Mazurek, 1995).

3.1.4 Reviews

In study somewhat similar to that presented here, Crawford and Savage (1994) reviewed the potential effects of alkaline plume migration for a Swiss radioactive waste repository in marl and crystalline rock types. They concluded that the effects would be manifested in terms of the closure of fractures and the channelling of groundwater flow. This would be accompanied by decreased matrix diffusion in the host rock and the loss of plasticity in bentonite seals. Radionuclide retardation would probably be increased as a result of the precipitation of zeolites and CSH phases, although this may be modified by competition from alkali and alkaline earth cations. They also noted that there was considerable potential for the generation of colloidal silica at the edge of the alkaline plume and the generation of organics from rock dissolution.

The sorption behaviour of a variety of metals on CSH has been reviewed by Tits (1994) and on zeolites by Valcke and Cremers (1995). Tits (1994) documents the incorporation of Cs, Sr and Ca (Lameille *et al.*, 1987), Cr (Cocke and Mollah, 1993), Np, La and Nd (Ewart *et al.*, 1990) in the CSH structure (co-precipitation). Bivalent ions substitute for Ca^{2+} and trivalent ions for Si^{4+}, in an analogous manner to Al^{3+}. Sorption sites on CSH can be either hydroxyl functional groups or negatively-charged surface sites due to substitution of Si^{4+} by Al^{3+}. Estimates of charge density of CSH vary from 80 to 140 meq.100 g-1, although charge density need not equate directly with exchange capacity. This CEC is considerably greater than that of illite and

comparable with that of smectite. K_d's for Cs on tobermorite are of the order of 1.4-1.51 m3 kg-1. Up to 92 % of Ca in tobermorite and 98 % of Ca in xonotlite can be replaced by Ni, Co, Sr and Ba.

Lagerblad and Trägårdh (1995), and Lagerblad (1996) discuss some aspects of cement-aggregate reactions as part of reviews of the potential for concrete deterioration for SKB. These authors concluded that aggregate-pore fluid reactions would decrease the porosity of cements placed in a deep groundwater environment, due to the formation of a non-swelling CSH gel, and in the long term, zeolites or feldspars.

3.2 Cement-aggregate reactions

Siliceous and carbonate rocks are used as aggregates in cement to produce concrete. Occasionally, excessive chemical reaction can take place between the aggregate and the concrete which manifests itself in terms of surface cracking or discolouration. Reactive forms of silica such as opal, chert, flint, volcanic glass and stressed quartz grains, or impure limestone or dolomite are often the culprits in such reactions. In silicate aggregates, alkali-aggregate reaction is caused by attack of the silicate framework of the mineral grains by alkali cations in the cement paste to produce a swelling alkali silica gel (Dent-Glasser and Kataoka, 1981). In dolomite, dedolomitisation reactions take place by dissolution of the dolomite by alkali cation attack and reprecipitation of calcite and brucite. These reactions have been studied extensively by researchers in the cement and concrete industry.

Solid volume expansion is noted in all studies of this type, across a range of aggregate types, such as basalt (Batic et al., 1994; Shayan et al., 1996), impure limestone (Grattan-Bellew, 1995); quartzite (Shayan et al., 1996), ignimbrite (Shayan et al., 1996), greywacké (Thomson and Grattan-Bellew, 1993; Hünger et al., 1994; Shayan et al., 1996), dolomite (Deng et al., 1993), opal (Baker and Poole, 1980), blast furnace slag (Gifford and Gillott, 1996), and chert and flint (Hobbs, 1993). In some cases, semi-mechanistic models have been developed to predict the mechanical effects of alkali-aggregate reaction (French, 1980; Hobbs, 1993; Léger et al., 1995; Sellier et al., 1995).

The reaction mechanisms for alkali-aggregate reaction are described both in generic terms (Bérubé and Fournier, 1986; Brouxel, 1993; Way and Shayan, 1993; Gillott, 1995) and for specific solids, such as, quartz (Kondo, 1967; Moorehead and McCartney, 1967; Henning and Gerstner, 1972; Baker and Poole, 1980), feldspar (van Aardt and Visser, 1977), opal (Baker and Poole, 1980), dolomite (Poole and Sotiropoulos, 1980; Deng et al., 1993), greywacké (Blackwell and Pettifer, 1992). Although the products of alkali-aggregate reaction are usually gels, zeolites have been identified as products in basalts (Batic et al., 1994) and unspecified aggregates (Marfil and Maiza, 1993), various Na-K silicates and hydrogarnets in feldspar-$Ca(OH)_2$ reactions (van Aardt and Visser, 1977), and a swelling silicate (probably smectite) in greywacké (Hünger et al., 1994).
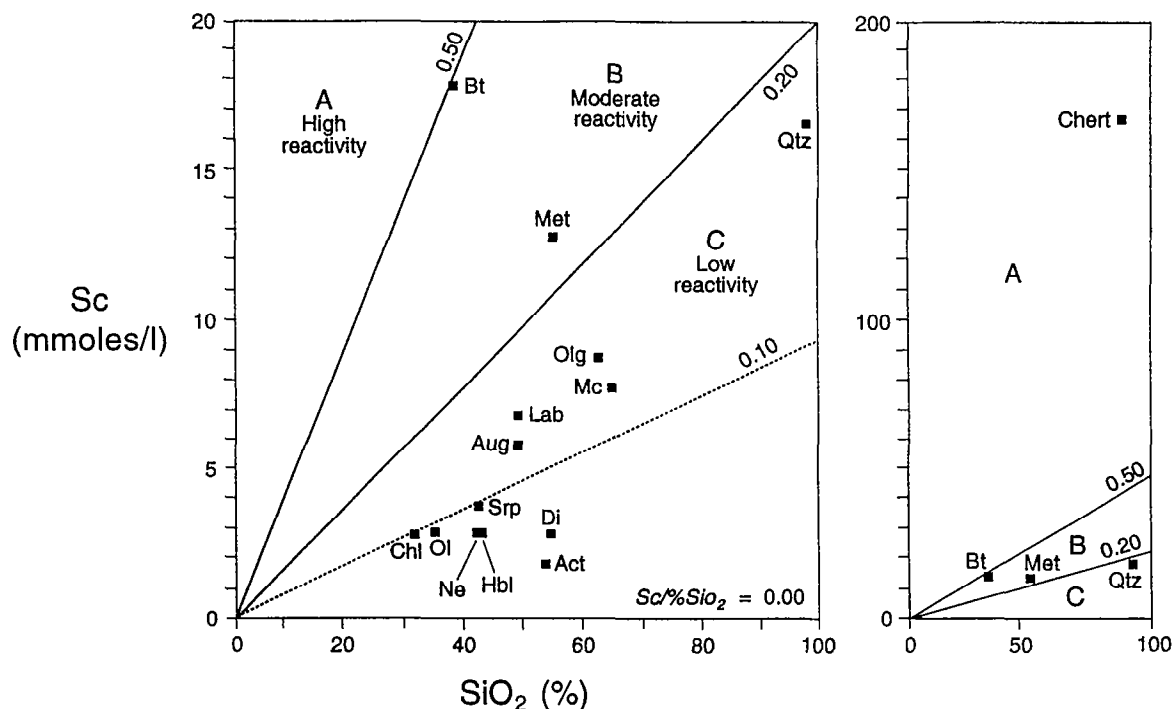
Figure 3.7 Plot of silica in solution (Sc) versus silica content of minerals derived from batch experiments at 80 °C carried out for 24 hours (from Choquette *et al.*, 1991). Minerals are designated 'high', 'moderate' or 'low' reactivity. Bt = biotite; Met = 'metabentonite'; Qtz = quartz; Olg = oligoclase feldspar; Mc = microcline feldspar; Lab = labradorite feldspar; Aug = augite (pyroxene); Chl = chlorite; Srp = serpentinite; Ol = olivine; Ne = nepheline; Hbl = hornblende; Act = actinolite.

Some of these studies afford an assessment of the different rates of mineral reactivity during alkali attack (Krzheminskii *et al.*, 1967; Kondo and Ohsawa, 1979; Poole and Sotiropoulos, 1980; Choquette *et al.*, 1991; Thomson and Grattan-Bellew, 1993). For example, Choquette *et al.* (1991) noted that of a suite of minerals investigated, chert was the most reactive, followed by biotite, metabentonite (*sic*), quartz and feldspars (Figure 3.7). Iron and magnesium silicates such as chlorite, olivine, serpentine, hornblende, actinolite and diopside were unreactive, whereas dolomite, siderite and gypsum were highly reactive.

A feature of some alkali-aggregate reactions of relevance to radioactive waste disposal is the potential for the release of Na and K from the rock due to exchange of Ca^{2+} ions in the cement paste for alkali cations in the silicate glass/mineral in the rock. In a repository context, this has the potential to extend the migration of the alkaline plume and increase the pH of migrating pore fluids. Na/K release from the rock has been identified for basalts (Batic *et al.*, 1994; Goguel, 1995), impure limestones (Grattan-Bellew, 1995), and dolomite (Poole and Sotiropoulos,

1980).

In one instance, release of organics surrounding aggregate grains derived from alluvial gravels has been documented (Eglinton et al., 1994). This caused staining and insufficient cementation of the resulting concrete.

3.3 Hydrocarbon reservoir remediation

Alkalis are injected into oil reservoirs to decrease oil-water interfacial tensions and thus to increase oil recovery (Cooke et al., 1974). Alkali-rock (usually sandstone) reactions accompany these processes which lead to undesirable loss of alkali. The oil industry has conducted research to study and minimise alkali-rock reaction during oil recovery. Much of the published research is experimental and/or modelling studies to interpret laboratory core flood experiments. Typically, these experiments consist of the injection of NaOH/KOH brines through sandstone cores, determining the chemical composition of output fluids with time, and rarely, mineralogical characterisation of the products. Considerable effort has been placed upon the development of computer models to predict the rate and absolute amounts of alkali loss.

Some studies emphasise mineral (principally clay) ion exchange reactions only as the process by which alkali is consumed in the sandstone reservoir (Cooke et al., 1974; Jennings et al., 1974; deZabala et al., 1982; Somerton and Radke, 1983; Bunge and Radke, 1983, 1985; Novosad and Novosad, 1984). However, Bunge and Radke (1982) were the first to recognise that ion exchange was responsible for the delay in arrival of the alkali pulse in core flood experiments, whereas mineral dissolution-precipitation reactions caused the overall depletion of OH- in output fluids (Figure 3.8). Mineralogical characterisation of rock cores post-experiment is not a feature of most studies, although a number of authors refer to zeolite products (Sydansk, 1982; Bunge and Radke, 1982; Mohnot et al., 1987; Thornton, 1988) and one to calcium silicate hydrates (Hughes et al., 1995). Bryant et al. (1986) emphasised the need to address both ion exchange and mineral dissolution-precipitation reactions to model alkali migration quantitatively.

Surprisingly, there are few references to porosity and permeability changes due to alkali-rock reaction. Bazin and Labrid (1991) note porosity decreases in a sandstone core in a laboratory core flood experiment due to carbonate precipitation from an injected K_2CO_3 fluid. Hughes et al. (1995) record increases in solid volume in batch experiments with single mineral isolates and cement leachates. In a field test of alkali flooding, Cooke et al. (1974) noted decreased porosity in the production well due to scaling with calcite, caused by mixing of the alkaline water with the indigenous formation fluid. Sydansk (1982) carried out laboratory core flooding experiments at 85 °C on a variety of sandstones with 4 wt % NaOH and noted porosity increases for all samples. The dissolved silicon content of effluent fluids ranged up to 16.5 g kg^{-1}. The porosity change ($\emptyset_{final}/\emptyset_{initial}$) was in the range 1.06-1.10 for 10 pore volumes flooded (initial porosities in the range 14-19 %) and up to 1.60 for 100 pore volumes (initial
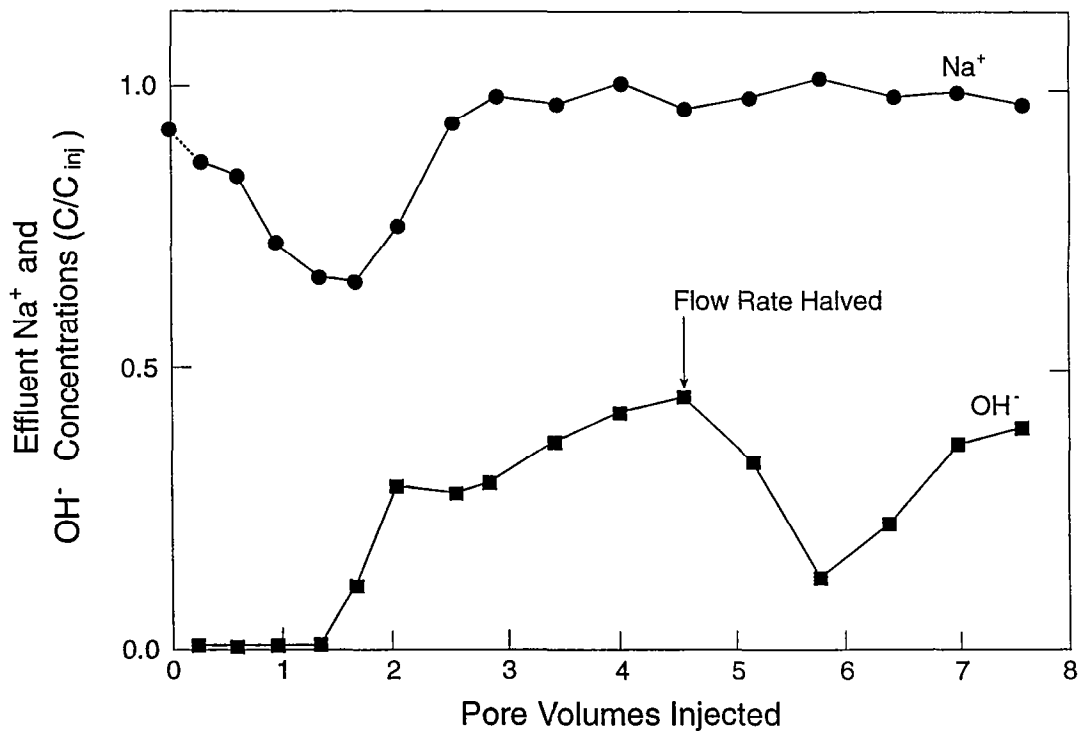
Figure 3.8 Concentration of Na+ and OH- in effluent from passing 0.04 M NaOH through a Berea Sandstone core at 23 °C (from Novosad and Novosad, 1984). Note the delay in produced OH- which did not meet the inlet concentration after 4.5 pore volumes. The decrease in Na+ output up to ~ 3 pore volumes is attributed to uptake on the rock, corresponding to 0.4 meq/100 g of rock. When the injection flow rate was halved, the effluent sodium concentration remained unchanged (indicating saturation of exchange sites), whereas the pH decreased, indicating an additional mechanism of OH- consumption (due to mineral dissolution).

porosities in the range 19-21 %). However, this increase in porosity was not always accompanied by an increase in permeability. The precipitation of zeolites in pore spaces often decreased permeability after reaction.

The recognition that the amount of alkali loss during recovery processes is due to slow mineral dissolution-precipitation reactions has, in some studies, prompted the need to quantify the rates of mineral dissolution (Sydansk, 1982; Bunge and Radke, 1982; Somerton and Radke, 1983; Mohnot et al., 1987; Krumrine and Falcone, 1988). At 70 °C, Bunge and Radke (1982) note the following sequence of decreasing release of Si to solution from mineral dissolution: amorphous silica > Ottawa Sand > kaolinite > montmorillonite > K-feldspar > biotite (Figure 3.9). Thornton (1988) also investigated Si release and observed the following order at 24 °C: muscovite > microcline > albite > quartz > biotite > chlorite, and the following at 70 °C: quartz
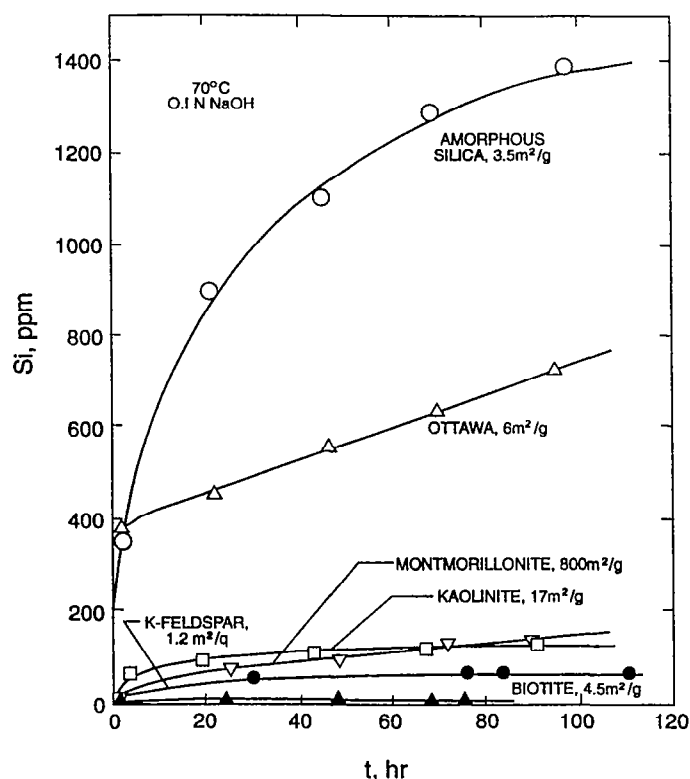
Figure 3.9 Change of Si fluid concentration with time for various minerals in batch experiments at 70 °C (from Bunge and Radke, 1982). The solution volume to solid mass ratio was 200 cm³ g⁻¹.

> microcline > albite > muscovite > biotite > chlorite. Mohnot *et al.* (1987) report results for the *loss of alkalinity* (at 82 °C in 5 % NaOH), decreasing in the sequence: kaolinite > montmorillonite, illite > quartz. This latter study incorporates alkalinity loss through precipitation as well as dissolution reactions.

Numerical models of varying complexity have been developed to simulate processes of alkali-rock reaction. Some of these address only ion exchange (deZabala *et al.*, 1982; Bunge and Radke, 1983, 1985), or kinetically-driven mineral dissolution (Krumrine and Falcone, 1988), whereas others incorporate both ion exchange and equilibrium dissolution-precipitation reactions (Bryant *et al.*, 1986; Bazin and Labrid, 1991), and a few incorporate ion exchange and rate-limited mineral dissolution (Bunge and Radke, 1982). None of the models addresses changing porosity-permeability with time, spatial heterogeneity, reactions in 2-D, or migration of solid particulates. Most of these models simulate alkali injection processes reasonably well, despite the omission of important processes in one or more cases. However, it should be realised that laboratory or field injection tests may be of the order of days to months, rather than the much longer timescales envisaged for radioactive waste isolation.

3.4 Others

This category includes references relating to soil stabilisation, sediment diagenesis, the assessment of clay liners for landfills, and paper pulping processes.

Soils may be stabilised from erosion and to improve mechanical behaviour by treatment with lime. Pozzolanic reactions between silicate/aluminosilicate minerals in the soil and the lime form insoluble phases which bind mineral grains together. Bérubé et al. (1990) carried out laboratory experiments at 25 and 80 °C to assess the reactivity of a large range of mineral types to attack by $Ca(OH)_2$. At 25 °C, opal, chert and metabentonite, nepheline and dolomite were all highly reactive, oligioclase (feldspar) and quartz were reactive, whilst all other minerals were unreactive. At 80 °C, CSH and CASH minerals/gels were identified as products on most aluminosilicates, whereas brucite and calcite were observed as products of dolomite reaction. Kobashi (1967) reacted the clay minerals allophane and kaolinite with $Ca(OH)_2$ at 30 °C and found gehlenite hydrate as a product in all experiments.

There has been some research of alkali reactions from a perspective of sediment diagenesis. Carroll and Starkey (1971) noted that kaolinite was more reactive than montmorillonite, metabentonite and illite during attack with 2.5 M NaOH at 25 °C. However, Golden et al. (1985) found that smectite could be produced by heating palygorskite with NaOH at 150 °C. They also observed the formation of smectite and analcime by treating sepiolite with NaOH. In contrast, Eberl et al. (1993) document the conversion of smectite to illite at 35-60 °C in solutions of KOH and NaOH in experiments up to 270 days duration.

The effect of alkalis on clays is relevant to the performance of clay liners used in landfills. Lentz et al. (1985) carried out permeability measurements on kaolinite, kaolinite-bentonite and Mg-montmorillonite for 30 days using NaOH (pH = 9, 11 and 13) as a permeant at 25 °C. No permeability increases were observed for any of the clays after the passage of 6 pore volumes of NaOH, but there was a reduction in permeability by a factor of 13 in the pH 13 experiment with Mg-montmorillonite. Lentz et al. attributed this to the precipitation of brucite in the clay pore space due to ion exchange of Na from the fluid for Mg on the clay. Brucite was not characterised mineralogically after the experiment.

Scaling of process equipment in paper pulping mills can occur due to alkali-silicate reactions. Frederick et al. (1986) investigated these reactions with experiments at 95 and 150 °C. Sodalite and other zeolites were found to be important in limiting the concentrations of Si and Al. In the presence of Ca, aluminous tobermorite or sodalite occurred. Hydrotalcite was an important product in the presence of Mg.

Richardson et al. (1986) reacted kaolinite, illite and montmorillonite with NaOH at room temperature and in a microwave process to investigate methods of 'cleaning' coal of clay minerals. No solid products were formed at 25 °C, but hydroxysodalite formed from kaolinite and zeolites from montmorillonite in the microwave process.

3.5 Summary

Points arising from the literature review for certain key issues for the disposal of radioactive wastes are summarised below.

3.5.1 Spatial scale of alkaline alteration

Modelling studies have calculated a range for the extent of the alkaline alteration, from ~ 5 m after 10^2 years, to 1000 m over 10^4 years. These studies encompass different conceptual assumptions and numerical methods to arrive at these estimates. Although models such as MPATH, CHEQMATE, and PRECIP provide reasonable (predictive) simulations of the types and sequences of alteration minerals to be expected along flowpaths affected by plume migration (in comparison with alteration observed at Maqarin), it is unlikely that any of these models currently provide realistic estimates of the extent of the alkaline alteration to be expected around a cementitious repository.

Column experiments are generally viewed as the most appropriate means by which models of reaction and flow can be tested because of well-constrained boundary conditions (temperature, starting materials, flow rate). However, the high porosities of rock/mineral columns and relatively high flow rates ensure that alteration in these experimental systems is dominated by the chemical composition of the input fluids. In repository systems, reaction will be rock-dominated because of low permeabilities and low groundwater flow rates. Consequently, the type of alteration observed in column experiments may be substantially different from that to be expected in repository systems. Greater contributions from elements such as Si, Al, and C which will be sourced from the rock and fracture linings will be apparent in alteration around radioactive waste repositories. Zeolites, feldspars, and calcite may thus be more important than alteration observed from previous column experimental studies.

Maqarin currently provides little quantitative information on the likely extent of the alkaline plume for most repository situations (Wellenberg excepted, possibly). Fundamental differences between Maqarin and most repository rocks in terms of physical properties and lithology mean that it is unlikely that the scale of alteration at Maqarin will be *directly* translatable to repository safety assessment.

3.5.2 Porosity and permeability

Qualitative evidence from radioactive waste experimental studies and cement aggregate investigations suggests decreases of porosity for all silicate/aluminosilicate mineral/rock types in both Na-K-Ca-OH and $Ca(OH)_2$ fluids, due to the rapid precipitation of Ca as CSH. Experiments involving NaOH or KOH without the presence of $Ca(OH)_2$ indicate the generation of porosity due to water-rock reaction. Thus there is an important distinction in results from

systems involving NaOH or KOH alone without admixed $Ca(OH)_2$ and those with $Ca(OH)_2$. However, since Ca will be rapidly removed from cement pore fluids migrating from a repository, groundwater flowpaths beyond the zone of CSH precipitation will effectively contact 'pure' NaOH/KOH. Whether these fluids create or destroy porosity is then a function of the growth kinetics of potential precipitates such as zeolites and feldspars. Laboratory experiments with relatively high concentrations of alkali hydroxide (*e.g.* Chermak, 1996) show that the growth of zeolites and feldspars is not kinetically hindered at reasonably realistic repository temperatures of 75 °C. The timescale over which the growth of zeolites and feldspars at lower temperatures and lower, more realistic, concentrations of alkali hydroxide occurs, remains an open question.

Decreases in rock porosity are predicted by radioactive waste modelling studies for both mixed alkali and calcium hydroxide fluids at distances from a few centimetres to a few metres from their source, whereas porosity increases have been calculated for mixed alkali hydroxide fluids close to the source (distances of a few centimetres). Although considerable uncertainty may accompany these estimates of distance, it is highly likely that there will be both zones of porosity creation and destruction along individual groundwater flow paths, according to variations in fluid composition due to mixing and reaction processes. The accuracy of these simulations depends to a large degree upon the availability of good kinetic (where appropriate) and thermodynamic data for solids such as CSH, CASH, and zeolites, as well as aqueous species of Al and Si.

With regard to reaction kinetics, synthesis of the quantitative and semi-quantitative data available from laboratory experimental studies suggests the following order of mineral reactivity at 80 °C: amorphous silica, dolomite, calcite > kaolinite > montmorillonite > quartz > K-feldspar > albite > chlorite, muscovite, biotite. At 25 °C, quartz is less reactive than at higher temperature, such that mineral reactivity is in the following sequence: amorphous silica, dolomite > quartz, feldspar > chlorite, biotite.

Analogue information from Maqarin suggests that Ca-dominated hyperalkaline fluids lead to porosity destruction and ultimately, the sealing of fractures, which thus provides good confirmation of experimental studies and model predictions for 'evolved' cement pore fluids. There is no relevant information available from Maqarin with reference to 'early' Na-K pore fluids.

3.5.3 Precipitation and co-precipitation

There is good evidence both from laboratory studies and/or the Maqarin natural analogue site for the precipitation of elements such as U, Cs, Sr, Cr, Np, La, Nd, Ni, Co, Ba, Th, Se, Pb with CSH and zeolites. Bivalent ions substitute for Ca^{2+}, and tri- and tetra-valent ions for Si^{4+}.

The absence of pH fronts at Maqarin hinders the understanding of changes in water chemistry and speciation at such features, but the occurrence of mineral reaction sequences in zoned

fracture fillings documents the passage of such fronts through the groundwater pathways at Maqarin.

3.5.4 Sorption

Laboratory evidence shows that sorption and ion exchange of many metal cations on CSH gels/minerals is high and in most instances should be greater than those observed for potential repository rocks. Sorption sites on CSH are either hydroxyl functional groups or negatively-charge sites due to the substitution of Si^{4+} by Al^{3+}. CSH have a high zero point of charge at elevated pH. Estimates of charge density on CSH is comparable with that of smectite.

Retardation on zeolites may be high for alkali metals (although competition for sorption sites from Na and K in cement pore fluids may be significant), but less favourable for tri- and tetra-valent metals. Sorption of actinide elements on zeolites is comparatively less well understood than on CSH.

3.5.5 Matrix diffusion

Evidence from Maqarin is somewhat equivocal. Alteration due to alkaline fluids is clearly visible in rocks adjacent to fluid filled fractures on the order of centimetres, but petrographic information shows that the matrix porosity is reduced due to the precipitation of calcite.

The precipitation of calcite due to fluid mixing has been predicted from model simulations of the diffusion of alkaline pore fluids into marl rock such that porosity sealing occurs over timescales of 10-100 years.

The reactions observed at Maqarin and predicted from modelling (i.e. the precipitation of calcite due to the mixing of hyperalkaline fluids with a neutral pH groundwater) would be expected to occur in most rock types. A reduction in porosity of the rock matrix due to calcite precipitation is thus likely, but may not preclude diffusion from groundwater-filled fractures.

3.5.6 Colloids

There is very little experimental information for the generation and characterisation of colloids in high pH fluids, although very high concentrations of Si in effluent fluids were noted in some oil industry sandstone core floods (of the order of 10 g kg-1). The occurrence of sharp pH fronts could thus lead to the development of large amounts of silica colloids due to the variation of silica solubility with pH.

Hyperalkaline groundwaters from Maqarin show low abundances of colloids, but pH fronts have not been identified.

3.5.7 Organics

Data from Maqarin and cement aggregate research suggests that organic materials can be readily dissolved and re-precipitated by alkaline alteration. This implies that any naturally-occurring organic materials in the host rock can be mobilised due to migration of the alkaline plume, and thus be available for complexation with radionuclides released from the repository.

3.5.8 Stability of clays

Laboratory experimental evidence exists to show that smectitic and kaolinitic clays are reactive (*i.e.* dissolution of the aluminosilicate framework occurs) in the presence of alkaline fluids (*e.g.* Bunge and Radke, 1982; Choquette *et al.*, 1991). The replacement of clays by brucite, C(A)SH minerals, illite and zeolites is documented from these studies. The conversion of smectite to illite at low temperature (35-60 °C) over short experiment durations (~ 200 days) indicates that these reactions may not be kinetically hindered. This evidence suggests that bentonite seals employed in any repository may be degraded by reaction with cement and concrete, changing the porosity and swelling capability.

4. CURRENT AND FUTURE RESEARCH ACTIVITIES

Sources in various countries (Belgium, Canada, France, Germany, Japan, Spain, Sweden, Switzerland, UK, USA) were contacted for information relevant to alkali-rock reaction from a radioactive waste perspective. The summaries below consist of those from countries identified with active research programmes on this topic.

4.1 Japan

4.1.1 PNC

A literature survey of research relating to alkali-rock reaction in Japan carried out by PNC revealed no previous work on this subject, so an experimental study of bentonite alteration by cement pore fluid was initiated in 1996. The principal aim of these experiments is to establish the type of solid alteration products.

The bentonite experiments are being conducted in batch mode at 50, 80, 100 and 200 °C. Kunipia® bentonite, containing > 95 % Na-montmorillonite is the material studied in the experiments. Fluids employed include three concentrations of $Ca(OH)_2$ to maintain pH at 10.5, 11.5 and 12.5, together with 1.0 M NaOH (pH = 14). At pH 12.5, degradation of the montmorillonite structure was identified from XRD data, and solid products of calcium aluminium hydrates (50 °C) and calcium silicate hydrates (80, 100 °C) were identified. At pH 10.5, and 11.5, calcium was consumed from the fluid phase, but no secondary solids were identified after 180 days of reaction. At 200 °C, montmorillonite was converted to analcime at pH 14 after one week, but remnants of montmorillonite were still identified after 170 days at pH 12.5 at 200 °C. It is anticipated that a model for bentonite alteration by a high-pH plume will be developed from this work. Further experiments are planned to investigate the effects of different experimental conditions on bentonite alteration and the interaction of rocks with cement pore fluids.

Experiments with rock and cement pore fluids will be carried out under six tasks:

(1) batch experiments to investigate rock alteration by cement pore fluids (granite from Kamaishi mine reacted with 0.001 M $Ca(OH)_2$ and 0.1M NaOH + 0.1 M KOH + 0.001 M $Ca(OH)_2$ at 80 °C and a 1:1000 g/ml ratio);

(2) batch sorption tests using Cs and I on altered rock;

(3) column experiments to evaluate changes in rock porosity, permeability and dispersion by alkaline alteration;

(4) prediction of the results of tracer tests in rock columns using the information gained

under tasks (1)-(3);

(5) tracer tests using columns of altered and unaltered rock;

(6) estimation of the effects of alkaline alteration of rock upon radionuclide migration.

This experimental programme was initiated in August 1996 and is scheduled for completion by late-1997.

4.1.2 Japanese Gas Corporation (JGC)

Activities are focussed on three areas.

Bentonite-alkali reactions. A series of batch experiments is being carried out to understand how montmorillonitic clay could alter in alkaline fluids. Almost pure montmorillonite (Kunipia F) has been reacted with 0.3 M NaOH or 0.3 M Ca(OH)$_2$ under an aerobic atmosphere at various temperatures (60, 90, 120, and 180 °C) for periods of 1, 3 and 6 months. In the NaOH solutions, analcime was identified by XRD as a product after one month at 90, 120 and 180 °C:

$$4NaOH + Al_4Si_8O_{20}(OH)_4 = 4NaAlSi_2O_6.H_2O \tag{4.1}$$

The pH (initially 13) did not change as a result of the experiments, except at 180 °C, when a decrease to pH 10 was measured. This suggests considerable consumption of NaOH to form analcime. In Ca(OH)$_2$, analcime was also observed as a product at 180 °C after one month's reaction. Further experiments are planned or have commenced:

- aerobic, batch experiments at 90 and 120 °C, using Kunigel VI, which consists of ~50 % Na-montmorillonite;

- batch experiments under anaerobic conditions;

- column experiments using cement-equilibrated water to investigate bentonite alteration in a dynamic system;

- batch sorption tests using Cs and Tc on altered montmorillonite.

Potential effects of the alkaline plume on the near-field rock. A literature survey has been carried out on this topic in order to assess which phenomena are important and how they might be incorporated into performance assessment. There is currently no experimental work associated with this programme.

Modelling. A code called ARASE ('rough wave' in Japanese) has been developed between

JGC and QuantiSci Ltd. ARASE couples chemical reactions and transport in two dimensions and is capable of dealing with kinetically-driven reactions. Demonstration calculations of the simulation of cement-rock-bentonite interactions in 2-D have been carried out.

4.2 Sweden (SKB)

SKB's interests are focussed on the following topics.

4.2.1 Influence of high pH on flow porosity

Fritz and co-workers (Fritz *et al.*, 1988; Fritz and Madé, 1991) investigated the potential influence of high pH from concrete on the porosity of granitic rock. Geochemical calculations were made with the codes DISSOL, THERMAL, and KINDIS (discussed elsewhere in this report).

4.2.2 Effects of concrete on bentonite behaviour

Interaction between concrete and bentonite have been discussed in connection with the Final Safety Report of the SFR facility. The silo is made of concrete and surrounded by a backfill of bentonite clay. Coupled calculation models (geochemical reactions and diffusion transport) were applied to the interaction of bentonite and concrete (Rasmuson *et al.*, 1988). The opposite reaction of high pH on bentonite was also considered, but with the very conservative assumptions of stoichiometric hydrolysis of the clay. Coupled models were not needed for this assessment and it was concluded that the bentonite would last for as long as deemed necessary (1000 years), considering the source of relatively short lived waste (low and intermediate level waste from reactor operations, *e.g.* spent ion exchange resins).

The potential interaction between bentonite clay and concrete is relevant to other possible applications in Sweden, such as the use of plugs and sealings, and in 1990 an initiative was taken to participate in a jointly supported (Nagra and SKB) experimental programme on concrete/bentonite interaction. The experiments were performed by Clay Technology in Sweden and calculations were made by Bertrand Fritz and co-workers in France. The tests have been concluded and evaluated, and the results will be reported in a Technical Report. The bentonite has been relatively insensitive to the influence of concrete in contrast to earlier conservative assumptions used in performance assessment.

4.2.3 High pH solutions in granitic rock

Interest in reactive transport of high pH-solutions in granitic rock (*i.e.* bed rock of 'granitic'

composition, and thus not necessarily granite *sensu stricto*) is focused on the use of bentonite in a spent fuel repository and whether it is necessary to restrict the use of concrete or not. From a construction point of view it would be advantageous to be able to use concrete, for example, for paving, shotcreting, injection, plugging, underground constructions *etc*. Important questions are: is it possible to use ordinary Portland cement, how much, and at what distance from the canister positions? Part of the answers are sought in the reactive transport of high pH solutions in granitic rock (above), which is one reason for the participation of SKB in the jointly supported (with Nagra and Nirex) column experiments being performed at the British Geological Survey (Bateman *et al.*, 1995).

A separate initiative to assess the potential effects of high pH from concrete has been made based on a hypothetical case with a concrete paved tunnel above bentonite filled deposition holes. Geochemical calculations were performed by WS Atkins Environment. The results have not yet been included in any technical report.

4.2.4 High pH and radionuclide retention

An initiative to study the influence on matrix diffusion (diffusion of radionuclides into the connected porosity of microfractures in seemingly intact rock) has been undertaken. Laboratory experiments are being carried out in cooperation between BGS (rock-water interaction and characterisation) and Chalmers University (radionuclide diffusion).

4.2.5 Behaviour of aggregates in concrete

Concrete is a mixture of cement and rock (aggregate), so the interaction of high pH porewater on silicate rich rocks can be followed by studying samples of old concrete which have been water saturated (Lagerblad, 1996). However, the main emphasis of these studies is directed at the longevity of the concrete material. Conservative assumptions of the behaviour of concrete structures have been made in the past, so SKB would like to be more realistic in future safety assessments. A summary of know-how in this field has been put together by the Cement and Concrete Research Institute, CBI, in Stockholm (Lagerblad and Trägårdh, 1995).

4.2.6 Natural analogues

SKB has participated in Phases II and III of the Jordan natural analogue project and continues to be interested in studies of this type.

4.3 Switzerland (Nagra)

4.3.1 'Black box' experimental work

A series of so-called 'black box' microcosm experiments were set up at BGS to investigate long-term interactions between repository components (cement, canister metal, ion exchange resins), a marl host rock, groundwater and microbiology (Milodowski et al., 1994). From this suite of experiments, three of the initial eight cells were opened after approximately 56 months of reaction at room temperature. The solid materials (marl and cement) and the cell precipitates ('sedimented sludges') were characterised by an integrated mineralogical and petrographic study in order to detect the mineralogical alteration products. Information from these studies was intended to fill the gap between normal short-term laboratory experiments (of approximately 3 months duration) and real long-term interactions of hyperalkaline pore fluid with marl (the potential host rock for a Swiss repository for low and intermediate level waste).

4.3.2 Column experiments (jointly funded by Nagra, Nirex and SKB)

A suite of column experiments was conducted at BGS to derive spatial and temporal fluid chemical and mineralogical data as a means to test coupled chemical and flow computer codes developed to model the migration of a hyperalkaline fluid plume from a deep geological repository. During these experiments, single minerals of importance to the radioactive waste disposal programmes in the UK, Sweden and Switzerland were reacted with 'young' (Na-K-Ca) hydroxide synthetic cement pore fluid and with evolved Ca-hydroxide fluids which will be formed during cement alteration. An experimental temperature of 70 °C was selected as a compromise between likely disposal temperatures and the elevated temperatures necessary in order to achieve results on a reasonable laboratory timescale (5 months). Mineral samples of quartz, albite, muscovite and calcite were prepared and characterised using SEM and electron microprobe.

A second series of laboratory column experiments is underway using the same experimental conditions as used in Phase I. In Phase II the experimental set up uses only a synthetic 'young' pore fluid with Na-K-Ca-OH composition in order to generate spatial and temporal data on fluid chemical and mineralogical changes and to increase confidence in coupled chemistry and flow computer models. Besides potential host rock lithologies of the participating parties (marl, Borrowdale Volcanic Group, granite, material from the Maqarin site and Opalinus Clay), simplified synthetic representations of the rocks have been assembled in order to provide more tightly constrained parameters for comparison with the codes. Separate experiments using monomineralic columns (quartz) in which only one predefined parameter is changed are set up in parallel to allow sensitivity studies and more straightforward modelling work to be carried out.

4.3.3 Research at the Paul Scherrer Institute

For several years, as part of the Swiss national research programme, sorption studies with safety relevant nuclides on different materials/media have been carried out. These studies covered and still cover the experimental and the modelling research related to the near field and far field of repositories for low, intermediate level, 'TRU' (waste containing transuranic elements) and high level waste.

Experimental work on sorption kinetics and sorption isotherms for safety relevant radionuclides on single and secondary mineral phases expected in altered marl are ongoing. These studies include laboratory and literature research focused on the properties of cement and its alteration products, diffusion of radionuclides through cement, and the influence of various organic materials on its sorption properties. An experimental programme on colloids associated with cement (generation, behaviour and fate) has also begun. The overall work includes not only 'data collection' for several sorption databases, but also the build up of a sufficiently detailed understanding of sorption processes so that any simplified description of sorption used subsequently in performance assessment studies can be justified and made transparent.

The research work mentioned above is part of a long-term programme which will be kept ongoing in order to improve the understanding of sorption mechanisms especially under hyperalkaline conditions. Techniques will also include the use of surface analytical techniques to study important mineral sorbants.

4.3.4 Research at the University of Bern

Laboratory experiments reacting Opalinus Clay and Palfris mudstone with hyperalkaline fluids at a variety of temperatures have been carried out. These studies have been supported by modelling work using the MPATH code.

Nagra's participation in Phases I-III of the Maqarin natural analogue site have been organised through the University of Bern. Sampling of groundwaters for colloids and geochemical model testing has been carried out.

4.3.6 In situ experiments

Experiments involving sources of alkali metal hydroxides are planned for both the experimental tunnel at Mont Terri (in Opalinus Clay) and during Phase V of the Grimsel Project (in granite). These latter experiments will involve the use of solid sources of NaOH/KOH, $Ca(OH)_2$, and mixed Na-K-Ca-OH, together with radioelement tracers, to be sealed in boreholes for up to 5 years. Reactions with the host rock and groundwater will be monitored in adjacent boreholes and by over-coring after experiment completion.

4.4 United Kingdom

4.4.1 Environment Agency

Research funded by the Environment Agency has emphasised the long-term behaviour of cement and concrete in the repository environment rather than alkali-rock reaction. With regard to the latter, the Agency has focussed its attentions on participation in Phase III (1994-1996) of the Maqarin Natural Analogue Project. Within this project, the Agency has funded QuantiSci Ltd. to carry out a review of zeolite behaviour and modelling of mineral stability and groundwater compositions at the Maqarin site (Savage, 1996). This work was concluded in November 1996.

The Agency has co-funded the study presented here in order to better focus its future research requirements with regard to issues concerning alkaline plume migration.

4.4.2 UK Nirex Ltd.

Nirex has used a multi-faceted approach to address the issue of alkaline plume migration:

- laboratory experiments (at the British Geological Survey) to investigate reaction mechanisms and rates of reaction of single minerals, rocks, and fracture fillings with alkaline fluids to investigate mineralogical alteration associated with plume migration;

- laboratory experiments (at AEA Technology) to determine changes (if any) to the diffusion properties of specimens of Borrowdale Volcanic Group rocks as a result of alkaline alteration;

- involvement in studies at the Maqarin Natural Analogue site in Jordan;

- computer modelling (carried out by the British Geological Survey and AEA Technology) to assess the extent of plume migration and changes to rock physical properties;

- laboratory experiments (at AEA Technology) to determine the change in rock sorption properties due to alkaline plume migration.

Laboratory experiments have been used to derive quantitative data concerning reaction mechanisms and rates of dissolution-precipitation, diffusion and sorption processes and to extrapolate those to larger spatial and temporal scales using numerical modelling. Information from the natural analogue site at Maqarin provides information over the longer term for mineral alteration, plume extent and matrix diffusion processes. Laboratory experiments have also been used to 'age' rock specimens for further experimental work to investigate sorption or diffusion

properties. No experiments have been conducted to investigate porosity-permeability changes to fractured rock systems.

Modelling of 2 types has been conducted:

- reaction-path modelling of closed (batch), principally experimental, systems;

- coupled reaction and transport modelling (in 1-D) of experimental and theoretical systems using the CHEQMATE, CHEQFRAC, MARQUISS and PRECIP codes.

In these studies it has been determined that kinetic mechanisms and rates of reactions are required in order to be able to model mass transfer on the order of 10's metres. Access of the fluid to the rock matrix and its impact on mineralogical alteration is currently being investigated. A number of inter-code comparison exercises between CHEQMATE, PRECIP and MARQUISS has been conducted, which has shown good agreement between the results of the models, despite large differences in numerical and conceptual differences between the codes.

CHEQMATE and PRECIP are currently being employed to model the evolution of a complex mineral assemblage, consisting of quartz, muscovite, K-feldspar, calcite and dolomite, which is representative of BVG lithologies at the Sellafield site. The size of the alteration zone was predicted to be less than a few metres after 1000 years; although the results in detail are affected by uncertainties concerning the kinetics of mineral reactions, particularly the silicates. However, the spatial extent of the plume of hyperalkaline groundwater is greater than the zone of extensive mineral reactions. Dolomite is particularly important for reducing pH in the fractures.

Trends in porosity changes caused by plume migration have been estimated. If carbonates dominate the fracture paths, then porosity increases are predicted for 'early' pore fluids. If silicates dominate, then porosity decreases are expected. At longer timescales, porosity is predicted to reduce regardless of reactant mineralogy, with a hypothetical near-field pore fluid. Nirex conclude that the alkaline disturbed zone will be a volume of lower permeability than the surrounding unperturbed rocks.

Experimental results indicate that actinide (U, Pu, Th) retardation in the alkaline disturbed zone will be greater than, or comparable to, that in the undisturbed geosphere (Berry, 1996). This has been explained by preferential sorption of neutral or negatively charged aqueous actinide species by positively charged CSH solids (CSH solids have a zero point of charge of ~ pH 13). Silicates and iron oxides have zpc (zero point of charge) near neutral pH and are thus negatively charged at high pH and sorb actinides weakly under these condition. Cellulosic degradation products (up to 2×10^{-3} M isosaccharinate) have little impact on radionuclide partitioning. U and Pu sorption on 'aged' rock samples is stronger than unaltered rock, whereas Th sorption is unaffected by the alteration state of the rock.

Nirex regard data collection of mineral alteration and radionuclide retardation in hyperalkaline

groundwater as substantially complete. Uncertainty still exists regarding the physical properties of the disturbed zone, but reductions in porosity, permeability and matrix diffusion are predicted. Work at Maqarin has increased confidence in the results of the laboratory and modelling programme but has raised the issue of the importance of zeolites as alteration products. Work is in progress to clarify this in the form of long term column experiments. Preliminary calculations have been carried out to model the extent of hyperalkaline alteration around a repository in the BVG.

The presence of the alkaline disturbed zone around the repository has not been included in past safety assessment exercises due to a lack of relevant data. Future assessments will incorporate these effects. It is anticipated that future research will demonstrate that the alkaline disturbed zone will be limited in extent so that it will be possible to model this zone using an additional sub-model within the MASCOT PA code employed by Nirex. This sub-model would be parameterised using data describing sorption, rock matrix diffusion and the expected hydraulic properties of rocks reacted with high pH groundwaters.

4.4.3 University of Manchester

Dr Colin Hughes at the University of Manchester has interests in the interactions of hyperalkaline pore fluids with rock and engineered structures. In addition to participation in research programmes funded by UK Nirex Ltd., he has carried out research for Enterprise Oil involving experimental and mineralogical studies of cement-rock interactions (Hughes et al., 1995) and currently has a NERC-funded (Natural Environment Research Council) PhD studentship entitled: 'environmental geochemistry of cement/rock reactions around deeply buried engineered structures'. This studentship is held by Ms Emily Hodgkinson and is due for completion in 1997. The project involves both experimental studies of mineral-alkali reactions and mineralogical studies of both natural materials from Scawt Hill (Northern Ireland), Maqarin, Jordan, as well as archaeological materials from Hadrian's Wall.

In a second NERC-funded PhD studentship, Colin Hughes, with Professors Henderson and Greaves and Dr Clark is supervising a 'CASE' student at the Daresbury Laboratory, Sam Shaw, working on an experimental study of ordering and crystal growth in hydrous calc silicate gels.

5. IMPLICATIONS FOR PERFORMANCE ASSESSMENT

5.1 Key uncertainties

It is apparent from the previous sections, that there are some uncertainties which remain concerning understanding the migration and effects of an alkaline plume. These are summarised below.

5.1.1 Spatial scale of alkaline plume

Information to determine the extent of the alkaline plume comes from two principal sources: computer modelling; and natural analogues.

Estimates for the extent of the alkaline plume from computer modelling studies range from a few metres to kilometres. The different assumptions made in these simulations have contributed to the range of estimates produced. It is unlikely that any of the simulations carried out thus far provide a reliable estimate of the spatial extent of the alkaline plume because of the following limitations:

- all the modelling carried out has been conducted using one-dimensional flowpaths. This conceptual approach has limitations for understanding chemical reaction and transport in a fractured rock network. In the latter system, flow will be transferred to different fractures as individual fractures seal by mineral precipitation. Flow may thus be enhanced in fractures which remain open. Simulations in one spatial dimension cannot address this issue.

- spatial heterogeneity in the rock will lead to the development of non-planar reaction fronts (channelling or fingering of flow), which cannot be addressed in one dimension.

- since most of the rock-alkali reactions involve large solid volume changes, there needs to be a link between changing porosity/permeability conditions with time to the groundwater flow field. Not all model simulations have incorporated this feature.

- there are uncertainties in many of the relevant kinetic and thermodynamic data (C(A)SH solids, aluminosilicate minerals, aqueous Al and Si species) necessary as input to any numerical model. Studies to investigate the sensitivity of the simulation results to variations in key kinetic and thermodynamic parameters have not been published.

Analogue studies of alkaline alteration are currently focussed at Maqarin, Jordan. Differences in lithology, porosity, and permeability between Maqarin and potential repository rocks (Wellenberg, Switzerland excepted) make it unlikely that data concerning the scale of alteration

at Maqarin can be transferred *directly* to repository scenarios. However, analogue studies remain useful as a confirmation of alteration reaction mechanisms and potential changes to physical and chemical properties at repository sites (see below).

5.1.2 Porosity and permeability

Evidence from laboratory experiments, modelling, and natural analogue studies concur that alteration of aluminosilicate rocks by Ca-dominated hyperalkaline fluids will lead to decreases in rock porosity and permeability. Alteration of carbonate rocks/fracture fillings by $Ca(OH)_2$ may lead to slight increases of porosity (the replacement of calcite by portlandite has a solid volume decrease of ~ 5 %; the replacement of dolomite by calcite + brucite has a solid volume decrease of ~ 10 %).

Solid volume changes due to reactions with 'early' Na-K-Ca-OH cement pore fluids are less certain. Whilst Ca is present in these fluids along flowpaths, alteration (coupled with mixing with ambient groundwater) will probably lead to a porosity decrease. However, because Ca is rapidly removed as CSH, pore fluids migrating along flowpaths beyond the zone of CSH precipitation will predominantly consist of NaOH and KOH. The reaction of these Na-K-OH solutions with rocks may lead to extensive porosity creation (via dissolution of aluminosilicate and carbonate minerals), unless this is counterbalanced by precipitation processes (by zeolites and feldspars). Timescales over which the growth of zeolites and feldspars at repository temperatures and realistic concentrations of alkali hydroxide occurs, remain an open question. It is highly likely that there will be both zones of porosity creation and destruction along individual groundwater flow paths, according to variations in fluid composition due to mixing and reaction processes.

5.1.3 Sequence of mineral alteration

For systems dominated by evolved $Ca(OH)_2$-type fluids, there is reasonably good correlation between the broad sequence of mineral alteration observed in laboratory experiments, computer simulations and natural systems (Maqarin). However, the relationship of these mineral alteration sequences with distance along flowpaths (as tested by computer simulation of column experiments) is not predicted particularly well by currently available models. Developments and modifications to computer models and databases as suggested in Section 5.1.1 will help to improve this situation.

Although there is much evidence which suggests that the presence of small amounts of Ca in early Na-K dominated cement pore fluids will lead to porosity decreases during this phase of pore fluid composition (and thus perhaps producing favourable behaviour from a waste isolation perspective), the absence of confirmatory evidence from any relevant natural system remains a major uncertainty. All Na-K hyperalkaline systems of which the author is aware are

also accompanied by a high abundance of CO_2 (*e.g.* hyperalkaline lakes of the East African Rift System, intermontane basinal lakes in western USA). The presence of abundant CO_2 in these systems will thus produce a different style of alteration from that anticipated in repository situations.

5.1.4 Precipitation and co-precipitation

There is currently no natural system evidence for fluid chemical and speciation data accompanying precipitation processes at pH fronts. Evidence from the mineral record at Maqarin shows evidence of co-precipitation of a number of trace elements with CSH solids and zeolites. It would be extremely useful if potential sites for the occurrence of pH fronts at natural analogue sites could be identified for future sampling and analysis.

5.1.5 Sorption

Conclusions of experimental work carried out thus far are that sorption of radionuclides important to repository safety will be enhanced, or be no worse, in rocks altered by the migration of the alkaline plume, than in unaltered rock materials. Further work may be necessary better to understand sorption mechanisms at high pH and to study a wider range of radionuclides than those studied so far. Investigation of sorption on zeolites may require further study.

5.1.6 Matrix diffusion

It is not clear whether alkali-rock reaction will decrease or increase the diffusion of aqueous species from a fracture into the rock matrix. Mineralogical evidence from Maqarin shows evidence of both increasing and decreasing porosity in rock samples altered by diffusion of hyperalkaline fluids from fractures. Computer modelling of diffusion of hyperalkaline fluid from a fracture into the rock matrix demonstrates that matrix sealing by calcite precipitation should occur over timescales of 10-100 years.

5.1.7 Colloids

Although evidence from hyperalkaline groundwaters at Maqarin demonstrates that colloid abundances in these water types may be low, it is anticipated that the highest abundance of colloids would be found at pH fronts in the rock-groundwater system. The absence of identified occurrences of pH fronts at Maqarin means that the characterisation of colloid abundances at these features remains uncertain.

5.1.8 Stability of clays

Some laboratory experimental evidence (*e.g.* Bunge and Radke, 1982; Choquette *et al.,* 1991; Eberl *et al.,* 1993) shows that smectitic clays are one of the *relatively* more reactive mineral types in hyperalkaline fluids, indicating that the dissolution of smectite and its conversion to other mineral types (zeolites, micas) may not be kinetically hindered at high pH and relatively low temperature. However, other experiments show relatively less reaction of smectites, *e.g.* concrete-bentonite experiments conducted for SKB (F. Karlsson, *pers. comm.*). Reactions between smectite clays and hyperalkaline fluids may therefore warrant further experimental investigation.

5.2 Incorporation of the effects of alkaline plume migration into PA

It is apparent from the evidence summarised in this report that interactions between cement pore fluids and the host rock have the capacity to perturb the performance of the far-field as a barrier to radionuclide migration, potentially over long scales of time and distance. It is clear that these effects need to be assessed in performance assessment calculations.

Essential features which should be incorporated into performance assessment are the changes in properties/behaviour of the following in the zone affected by the alkaline plume:

- porosity-permeability of groundwater flowpaths;

- precipitation and co-precipitation (particularly at pH fronts);

- sorption;

- matrix diffusion;

- colloids;

- mobilisation of natural organics;

- cement-bentonite seals.

The anticipated effects of alkaline alteration upon these processes/properties is summarised in Table 5.1.

The effects of the perturbation of any or all of these processes/properties for waste containment may be minor if the zone of hyperalkaline alteration is small in physical scale. At this stage, it is unclear what the scale of alteration will be. Current estimates of the zone of alteration range

Table 5.1   Summary of the likely effects of alkaline plume migration on processes and properties important for radionuclide migration.

Process or Property	Likely Effect of Plume Migration
porosity and permeability of flowpaths	(1) 'early' Na-K-Ca-OH fluids, aluminosilicate flowpaths: a zone of net porosity-permeability increase may occur in the 'middle' of flowpaths , *i.e.* between zones of precipitates formed by groundwater mixing and those formed by water-rock reaction. Flowpaths may eventually be sealed due to CSH precipitation. (2) 'early' Na-K-Ca-OH fluids, carbonate flowpaths: extensive porosity/permeability increases will result from carbonate dissolution. (3) 'evolved' $Ca(OH)_2$ fluids: are likely to produce flowpath sealing in aluminosilicate rocks and minor porosity increases in carbonate rocks.
precipitation and co-precipitation	Radionuclides may be incorporated into both CSH and zeolites. Radionuclides moving in advance of the mineral precipitation front may be available for sorption on colloids forming at the pH front.
sorption	Current evidence suggests that sorption may be better, or no worse than that on unaltered rock for important radionuclides.
matrix diffusion	Unlikely to be better than unaltered rock and could be much worse.
colloids	Colloids may be generated at the pH front, but may have low abundances in high pH fluids.
mobilisation of natural organics	Organics will be dissolved from the rock where available to high-pH fluids.
cement-bentonite seals	Bentonite clay may be dissolved, zeolites and feldspars precipitated, producing a loss of plasticity and a reduction in porosity. Evolved $Ca(OH)_2$ fluids will exchange Ca^{2+} from the fluid for Na^+ on the bentonite, reducing swelling capacity.

from a few m to km. Performance assessors are thus faced with assuming either that the entire geosphere is perturbed by the plume or that the affected zone is limited in size. Better definition of the extent of alkaline alteration is dependent upon the translation of more relevant analogue data to PA and the development of more realistic models of alkali-rock reaction and transport.

It is recommended that geosphere sub-models are produced for PA with variations of the above processes/properties to scope the potential effects upon radionuclide migration with regard to a reference case which assumes little or no perturbation of the far-field due to alkaline plume migration.

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6. CONCLUSIONS

A number of key processes/properties affecting radionuclide migration has been identified which will be perturbed by the migration of a hyperalkaline pore fluid plume. These are: porosity and permeability; precipitation and co-precipitation behaviour; sorption; matrix diffusion; colloids; the mobilisation of organics from the host rock; and the behaviour of bentonite seals.

A review of literature pertaining to alkali-rock reactions in the radioactive waste, cement and concrete, oil industries, and elsewhere has been conducted. This has confirmed the existence of much relevant data concerning: alkali-rock reaction mechanisms and mineral alteration sequences; changes in porosity and permeability; sorption of radionuclides; matrix diffusion behaviour; the thermodynamics and kinetics of likely reactions; and the mobility of organics.

Countries with current and planned research activities on alkaline plume migration have been identified to include: Japan; Sweden; Switzerland; and the UK. These countries have many common interests in the issue of plume migration due to similarities in planned repository design, waste characteristics and potential repository host rocks. Therefore there is considerable potential for shared funding of research projects.

With regard to research carried out thus far, there are major uncertainties for performance assessment still remaining for: the overall spatial scale of alkaline alteration; the effects of 'early' Na-K dominated cement pore fluids; speciation-solubility behaviour of radionuclides at pH fronts; the mechanism of sorption behaviour in rock-water systems at high pH; matrix diffusion; colloid abundances at pH fronts; and the behaviour of bentonite at high pH.

Recommendations for performance assessment are that geosphere sub-models are produced for PA with variations of the above processes/properties to scope the potential effects upon radionuclide migration with regard to a reference case which assumes little or no perturbation of the far-field due to alkaline plume migration. Better definition of the scale of alteration is dependent upon the acquisition of better analogue data to repository scenarios and the use of more realistic models for chemical reaction and transport.

7.   REFERENCES

van Aardt, J.H.P. and Visser, S. (1977) Calcium hydroxide attack on feldspars and clays: possible relevance to cement-aggregate reactions. *Cement and Concrete Research* **7**: 643-648.

Alexander, W.R. (1995) Natural cements: how can they help us safely dispose of radioactive waste? Radwaste Magazine, **September 1995**: 61-69.

Alexander, W.R., Dayal, R., Eagleson, K., Eikenberg, J., Hamilton, E., Linklater, C.M., McKinley, I.G. and Tweed, C.J. (1992) A natural analogue of high pH cement pore waters from the Maqarin area of northern Jordan. II: results of predictive geochemical calculations. *Journal of Geochemical Exploration* **46**: 133-146.

Alexander, W.R. and Mazurek, M. (1995) The Maqarin natural analogue: possible implications for the performance of a cementitious repository at Wellenberg. *Unpublished Nagra Internal Report.*

Alexander, W.R., Smellie, J.A.T. and Crossland, I. (1996) Potential effects of hyperalkaline leachates on cementitious repository host rocks: an example from Maqarin, Jordan. Abstract for *Chemical Containment of Wastes in the Geosphere*, 3-4 September, Keyworth, Nottinghamshire, UK.

Atkinson, A. (1985) The time dependence of pH within a repository for radioactive waste disposal. *United Kingdom Atomic Energy Authority Report* **AERE-R11777**.

Atkinson, A., Everitt, N.M. and Guppy, R. (1987) Evolution of pH in a radwaste repository. Experimental simulation of cement leaching. *United Kingdom Atomic Energy Authority Report* **AERE-R12594**.

Baker, A.F. and Poole, A.F. (1980) Cement hydrate development at opal-cement interfaces and alkali-silicate reactivity. *Quarterly Journal of Engineering Geology London* **13**: 249-254.

Batic, O., Maiza, P. and Sota, J. (1994) Alkali silica reaction in basaltic rocks NBRI method. *Cement and Concrete Research* **24**: 1317-1326.

Bateman, K., Coombs, P., Noy, D.J., Pearce, J.M. and Wetton, P. (1995) Nagra/Nirex/SKB column experiments: results of experiments and modelling. *BGS Report* **WE 95/25C** ; *Unpublished Nagra Internal Report*, and *SKB Arbetsrapport* **AR 95-16**.

Bazin, B. and Labrid, J. (1991) Ion exchange and dissolution/precipitation modeling: application to the injection of aqueous fluids into a reservoir sandstone. *Society of Petroleum Engineers Reservoir Engineering*, **May 1991**: 233-238.

Berner, U.R. (1992) Evolution of pore water chemistry during degradation of cement in a radioactive waste repository environment. *Waste Management* **12:** 201-219.

Bérubé, M-A., Choquette, M. and Locat, J. (1990) Effects of lime on common soil and rock forming minerals. *Applied Clay Science* **5:** 145-163.

Bérubé, M-A. and Fournier, B. (1986) Les produits de la réaction alcalis-silice dans le béton: étude de cas de la région de Québec. *Canadian Mineralogist* **24:** 271-288.

Berry, J.A. (1996) The role of sorption onto the Borrowdale Volcanic Group in providing chemical containment for a potential repository at Sellafield. Abstract for *Chemical Containment of Wastes in the Geosphere*, 3-4 September, Keyworth, Nottinghamshire, UK.

Blackwell, B.Q. and Pettifer, K. (1992) Alkali-reactivity of greywacké aggregates in Maentwrog Dam (North Wales). *Magazine of Concrete Research* **44:** 255-264.

Braney, M.C., Haworth, A., Jefferies, N.L. and Smith, A.C. (1993) A study of the effects of an alkaline plume from a cementitious repository on geological materials. *Journal of Contaminant Hydrology* **13:** 379-402.

Brouxel, M. (1993) The alkali-aggregate reaction rim: Na_2O, SiO_2, K_2O and CaO chemical distribution. *Cement and Concrete Research* **23:** 309-320.

Bryant, S.L., Schechter, R.S. and Lake, L.W. (1986) Interactions of precipitation/dissolution waves and ion exchange in flow through permeable media. *American Institute of Chemical Engineering Journal* **32:** 751-764.

Bunge, A.L. and Radke, C.J. (1982) Migration of alkaline pulses in reservoir sands. *Society of Petroleum Engineers Journal,* **December 1982,** 998-1012.

Bunge, A.L. and Radke, C.J. (1983) Divalent ion exchange with alkali. *Society of Petroleum Engineers Journal,* **August 1983,** 657-667.

Bunge, A.L. and Radke, C.J. (1985) The origin of reversible hydroxide uptake on reservoir rock. *Society of Petroleum Engineers Journal,* **October 1985,** 711-718.

Carroll, D. and Starkey, H.C. (1971) Reactivity of clay minerals with acids and alkalies. *Clays and Clay Minerals* **19:** 321-333.

Chermak, J.A. (1992) Low temperature experimental investigation of the effect of high pH NaOH solutions on the Opalinus Shale, Switzerland. *Clays and Clay Minerals* **40:** 650-658.

Chermak, J.A. (1993) Low temperature experimental investigation of the effect of high pH KOH solutions on the Opalinus Shale, Switzerland. *Clays and Clay Minerals* **41:** 365-372.

Chermak, J.A. (1996) Interactions of the Palfris and Opalinus Shales with high pH NaOH and KOH solutions at 75 °C. *Unpublished Nagra Internal Report.*

Choquette, M., Bérubé, M-A. and Locat, J. (1991) Behavior of common rock-forming minerals in a strongly basic NaOH solution. *Canadian Mineralogist* **29:** 163-173.

Clark, I.D., Dayal, R. and Khoury, H.N. (1994) The Maqarin (Jordan) natural analogue for ^{14}C attenuation in cementitious barriers. *Waste Management* **14:** 467-477.

Cocke, D.L. and Mollah, Y.A. (1993) The chemistry and leaching mechanisms of hazardous substances in cementitious solidification/stabilisation systems. In *Chemistry and Microstucture of Solidified Waste Forms* (ed. R.D. Spence). Lewis, Boca Raton, 187-242.

Cooke, C.E., Williams, R.E. and Kolodzie, P.A. (1974) Oil recovery by alkaline water flooding. *Journal of Petroleum Technology* **December** 1365-1374.

Crawford, M.B. and Savage, D. (1994) The effects of alkaline plumes migration from a cementitious repository in crystalline and marl host rocks. *Unpublished Nagra Internal Report.*

Crompton, S., Grindrod, P., Takase, H. and Woods, J. (in press) Multibarrier geochemical problems in two spatial dimensions. Journal of Contaminant Hydrology.

Deng, M., Han, S.F., Lu, Y.N., Lan, X.H., Hu, Y.L. and Tang, M.S. (1993) Deterioration of concrete structures due to alkali-dolomite reaction in China. *Cement and Concrete Research* **23:** 1040-1046.

Dent-Glasser, L.S. and Kataoka, N. (1981) The chemistry of 'alkali-aggregate' reaction. *Cement and Concrete Research* **11:** 1-9.

deZabala, E.F., Vislocky, J.M., Rubin, E. and Radke, C.J. (1982) A chemical theory for linear alkaline flooding. *Society of Petroleum Engineers Journal* **April:** 245-258.

Eberl, D.D., Velde, B. and McCormick, T. (1993) Synthesis of illite-smectite from smectite at earth surface temperatures and high pH. *Clay Minerals* **28:** 49-60.

Eglinton, M.S., Higginbottom, I.E. and Pettifer, G.S. (1994) An unfamiliar alkali-aggregate reaction from Trinidad. *Quarterly Journal of Engineering Geology* **27:** 363-373.

Eikenberg, J. (1990) On the problem of silica solubility at high pH. *Nagra Technical Report* **NTB 90-36.**

Ewart, F.T., Glasser, F., Groves, G., Jappy, T., McCrohon, R., Moseley, P.T., Rodger, S. and Richardson, I. (1990) Mechanisms of sorption in the near-field. *UKDoE Report* **PECD**

Frederick, W.J. Jr., Streisel, R.C. and Gasteiger, H.A. (1986) The solubility of aluminosilicates in alkaline pulping liquors. *Chemical Engineering Technology in Forest Products Processing, AIChE Forest Products Division* 2: 67-80.

French, W.J. (1980) Reactions between aggregates and cement paste - an interpretation of the pessimum. *Quarterly Journal of Engineering Geology London* 13: 231-247.

Fritz, B. and Madé, B. (1991) Geochemical modelling of bentonite-alkaline solutions interactions in the near-field of a repository for spent nuclear fuel. *SKB Technical Report* 91-05.

Fritz, B., Madé, B. and Tardy, Y. (1988) Geochemical modelling of the evolution of a granite-concrete-water system around a repository for spent nuclear fuel. *SKB Technical Report* 88-18.

Gifford, P.M. and Gillott, J.E. (1996) Alkali-silica reaction (ASR) and alkali-carbonate reaction (ACR) in activated blast furnace slag cement (ABFSC) concrete. *Cement and Concrete Research* 26: 21-26.

Gillott, J.E. (1995) Review of expansive alkali-aggregate reactions in concrete. Journal of Materials in Civil Engineering **November 1995:** 278-282.

Goguel, R. (1995) Alkali release by volcanic aggregates in concrete. *Cement and Concrete Research* 25: 841-852.

Golden, D.C., Dixon, J.B., Shadfan, H. and Kippenberger, L.A. (1985) Palygorskite and sepiolite alteration to smectite under alkaline conditions. *Clays and Clay Minerals* 33: 44-50.

Grattan-Bellew, P.E. (1995) Laboratory evaluation of alkali-silica reaction in concrete from Saunders Generating Station. *ACI Materials Journal* 92 **(March/April):** 126-134.

Haworth, A. and Noy, D.J. (1995) Migration of a mixed alkali hydroxide solution in a fracture in crystalline rock. *UK Nirex Safety Series Report* NSS/R342.

Haworth, A., Sharland, S.M., Tasker, P.W. and Tweed, C.J. (1988) Evolution of the groundwater chemistry around a nuclear waste repository. In *Scientific Basis for Nuclear Waste Management, Vol XI*, Materials Research Society, 425-434.

Henning, O. and Gerstner, B. (1972) Untersuchungen zur Wechselwirkung zwischen Quarz und Kalziumhdroxid unter hydrothermalen Bedingungen. *Wissenschaftliche Zeitschrift der Hochschule für Architektur und Bauwesen Weimar* 1: 53-58.

Hobbs, D.W. (1993) Deleterious alkali-silica reactivity in the laboratory and under field conditions. *Magazine of Concrete Research* **45:** 103-112.

Hoyle, S.L. and Grutzeck, M.W. (1989) Incorporation of cesium into hydrating aluminosilicates. *Journal of the American Ceramic Society* **72:** 1938-1947.

Hughes, C.R., Hill, P.I. and Isaac, K.P. (1995) An experimental evaluation of the formation damage potential of cement filtrates and leachates. *Society of Petroleum Engineers* **SPE 30087:** 87-99.

Hünger, K-J., Wollgam, H. and Frey, R. (1994) Composition and structure of an iron/lime alkali layer silicate formed during greywake destruction. *Neues Jahrbuch für Mineralogie Monatsheft* **12:** 540-556.

Jefferies, N.L., Tweed, C.J. and Wisbey, S.J. (1988) The effects of changes in pH within a clay surrounding a cementitious repository. In *Scientific Basis for Nuclear Waste Management, Vol XI,* Materials Research Society, 43-52.

Jennings, H.Y.Jr., Johnson, C.E.Jr. and McAuliffe, C.D. (1974) A caustic waterflooding process for heavy oils. *Journal of Petroleum Technology* **December:** 1344-1352.

Khoury, H.N., Salameh, E., Clark, I.D., Fritz, P., Bajjali, W., Milodowski, A.E., Cave, M.R. and Alexander, W.R. (1992) A natural analogue of high pH cement pore waters from the Maqarin area of northern Jordan I: introduction to the site. *Journal of Geochemical Exploration* **46:** 117-132.

Kobashi, T. (1967) Reaction of calcium hydroxide with allophane-kaolinite clay minerals. *Clay Science* **3:** 11-36.

Komarneni, S., Breval, E., Roy, D.M. and Roy, R. (1988) Reactions of some calcium silicates with metal cations. *Cement and Concrete Research* **18:** 204-220.

Kondo, R. (1967) Kinetic study on hydrothermal reaction between lime and silica. In *Autoclaved Calcium Silicate Building Products,* Society of Chemical Industry, 92-100.

Kondo, R. and Ohsawa, S. (1979) Reactivities of various silicates with calcium hydroxide and water. *Journal of the American Ceramic Society* **62:** 447-449.

Krumrine, P.H. and Falcone, J.S. (1988) Rock dissolution and consumption phenomena in an alkaline recovery system. *Society of Petroleum Engineers Reservoir Engineering,* **February 1988:** 62-68.

Krzheminskii, S.A., Rashkovich, L.N., Sudina, N.K. and Varlamov, V.P. (1967) Influence of the composition of the mixture and the temperature of hydrothermal treatment on the kinetics

of interaction of lime and quartz. In *Autoclaved Calcium Silicate Building Products*, Society of Chemical Industry, 110-113.

Lagerblad, B. (1996) Conceptual model for the deterioration of Portland cement concrete in water. *SKB Arbetsrapport* **96-01**.

Lagerblad, B. and Trägårdh, J. (1995) Conceptual model for concrete long time degradation in a deep nuclear waste repository. *SKB Technical Report* **TR 95-21**.

Lameille, J.M., Goutiere, G., Petit, J-C. and Regourd, M. (1987) Retention of cobalt, cesium, and strontium in the hydrates of C_3S, C_3A, and gypsum. *Journal of the American Ceramic Society* **70**: 604-614.

Léger, P., Tinawi, R. and Mounzer, N. (1995) Numerical simulation of concrete expansion in concrete dams affected by alkali-aggregate reaction: state of the art. *Canadian Journal of Civil Engineering* **22**: 692-713.

Lentz, R.W., Horst, W.D. and Uppot, J.O. (1985) The permeability of clay to acidic and caustic permeants. In *Hydraulic Barriers in Soil and Rock*, (eds. A.I. Johnson, R.K. Froebel, N.J. Cavalli and C.B. Pettersson), *American Society for Testing and Materials*, 127-139.

Lichtner, P.C. and Eikenberg, J. (1994) Propagation of a hyperalkaline plume into the geological barrier surrounding a radioactive waste repository. *Nagra Technical Report* **NTB 93-16**.

Linklater, C.M., Albinsson, Y., Alexander, W.R., Casas, I., McKinley, I.G. and Sellin, P. (1994) A natural analogue of high pH cement pore waters from the Maqarin area of northern Jordan. In *Fourth International Conference on the Chemistry and Migration Behaviour of Actinides and Fission Products in the Geosphere*. Charleston, SC, USA, December 12-17, 1993, 639-644.

Lundén, I. and Andersson, K. (1989) Modeling of the mixing of cement pore water and groundwater using the PHREEQE code. In *Scientific Basis for Nuclear Waste Management, Vol XII*, Materials Research Society, 949-956.

Maqarin Natural Analogue Site Study Group (1991) A natural analogue study of the Maqarin hyperalkaline groundwaters. I. Source term description and thermodynamic database testing. *Nagra Technical Report* **NTB 91-10**.

Marfil, S.A. and Maiza, P.J. (1993) Zeolite crystallization in Portland Cement concrete due to alkali-aggregate reaction. *Cement and Concrete Research* **23**: 1283-1288.

Milodowski, A.E. (ed.) (1994) A natural analogue study of the Maqarin hyperalkaline groundwaters: a draft report on hyperalkaline groundwater/rock interaction. *Unpublished*

Nagra Internal Report.

Milodowski, A.E., Hughes, C.R., Kemp, S.J., Pearce, J.M., Prior, S.V. and Chenery, S.D. (1994) The mineralogy and petrography of altered starting materials and associated reaction products from the 'black-box' experiments: cells 2, 4 and 6. *Unpublished Nagra Internal Report.*.

Milodowski, A.E., Pearce, J.M., Hughes, C.R. and Khoury, H.N. (1992) A preliminary mineralogical investigation of cement-buffered hyperalkaline groundwater interaction with marl, Maqarin, northern Jordan. *Unpublished Nagra Internal Report.*

Mohnot, S.M., Bae, J.H. and Foley, W.L. (1987) A study of mineral/alkali reactions. *Society of Petroleum Engineers Reservoir Engineering,* **November 1987:** 653-663.

Moorehead, D.R. and McCartney, E.R. (1967) The mechanism of the quartz-lime solution reaction at temperatures up to 500°. In *Autoclaved Calcium Silicate Building Products*, Society of Chemical Industry, 86-91.

Nagra (1994) Kristallin 1 Safety Assessment Report. *Nagra Technical Report* **NTB 93-22.**

Novosad, Z. and Novosad, J. (1984) Determination of alkalinity losses resulting from hydrogen ion exchange in alkaline flooding. *Society of Petroleum Engineers Journal,* **February 1984,** 49-52.

Pearce, J.M., Alexander, W.R., Wetton, P.D. and Milodowski, A.E. (1996) A natural analogue study of the Maqarin hyperalkaline groundwaters: interim report on the production of colloids at the cement/host rock interface. *Unpublished Nagra Internal Report.*

Poole, A.B. and Sotiropoulos, P. (1980) Reactions between dolomitic aggregate and alkali pore fluids in concrete. *Quarterly Journal of Engineering Geology London* **13:** 281-287.

Rasmuson, A., Neretnieks, I. and Zhu, M. (1988) Calculations of the degradation of concrete in a final repository for nuclear waste. In *Near-field assessment of repositories for low and medium level radioactive waste.* Proceedings of a NEA workshop, OECD, Paris.

Richardson, C.K., Markuszewski, R., Durham, K.S. and Bluhm, D.D. (1986) Effect of caustic and microwave treatment on clay minerals associated with coal. In *Mineral Matter and Ash in Coal,* American Chemical Society, 513-523.

Rochelle, C.A., Bateman, K., Hughes, C.R., Pearce, J.M. and Savage, D. (1994a) The evaluation of chemical mass transfer in the 'disturbed zone' of a deep geological disposal facility for radioactive wastes. III. Reaction of Borrowdale Volcanic Group lithologies with Na-K-Ca hydroxide fluids. *Nirex Safety Series Report* **NSS/R327.** In preparation.

Rochelle, C.A., Bateman, K., MacGregor, R.M., Pearce, J.M., Savage, D. and Wetton, P. (1994b) The evaluation of chemical mass transfer in the 'disturbed zone' of a deep geological disposal facility for radioactive wastes. IV. The kinetics of dissolution of chlorite and carbonates at elevated pH. *Nirex Safety Series Report* **NSS/R368**. In preparation.

Rochelle, C.A., Bateman, K., MacGregor, R.M., Pearce, J.M., Savage, D. and Wetton, P. (1994c) The evaluation of chemical mass transfer in the 'disturbed zone' of a deep geological disposal facility for radioactive wastes. V. Reaction of powdered Borrowdale Volcanic Group lithologies with synthetic evolved near-field groundwater. *Nirex Safety Series Report* **NSS/R382**. In preparation.

Rochelle, C.A., Bateman, K., MacGregor, R.M., Pearce, J.M., Savage, D. and Wetton, P.D. (1995a) Experimental determination of chlorite dissolution rates. In *Scientific Basis for Nuclear Waste Management Vol XVIII*, Materials Research Society, 149-156.

Rochelle, C.A., Bateman, K., MacGregor, R.M., Pearce, J.M., Prior, S.V., Savage, D. and Wetton, P.D. (1995b) The evaluation of chemical mass transfer in the 'disturbed zone' of a deep geological disposal facility for radioactive wastes. VI. The hydrothermal aging of discs of bulk rock and near-fracture Borrowdale Volcanic Group lithologies with a synthetic evolved near-field groundwater. *Nirex Safety Series Report* **NSS/R390**. In preparation.

Rochelle, C.A., Bateman, K., Milodowski, A.E., Noy, D.J., Pearce, J., Savage, D. and Hughes, C.R. (1992) Reactions of cement pore fluids with rock: implications for the migration of radionuclides. In *Water-Rock Interaction*, (eds. Y.K. Kharaka and A.S. Maest), Balkema, Rotterdam, 423-426.

Savage, D. (1996) Zeolite occurrence, stability and behaviour: a contribution to Phase III of the Jordan Natural Analogue Project. *U.K. Dept of the Environment Report* **DOE/HMIP/RR/95.020**.

Savage, D., Bateman, K., Hill, P.I., Hughes, C.R., Milodowski, A.E., Pearce, J. and Rochelle, C.A. (1992a) The evaluation of chemical mass transfer in the 'disturbed zone' of a deep geological disposal facility for radioactive wastes. II. Reaction of silicates with Na-K-Ca hydroxide fluids. *Nirex Safety Series Report* **NSS/R283**. In preparation.

Savage, D., Bateman, K., Hill, P., Hughes, C., Milodowski, A., Pearce, J., Rae, E. and Rochelle, C. (1992b) Rate and mechanism of the reaction silicates with cement pore fluids. *Applied Clay Science* **7:** 33-45.

Savage, D., Hughes, C.R., Milodowski, A.E., Bateman, K., Pearce, J., Rae, E.I.J. and Rochelle, C.A. (1991) The evaluation of chemical mass transfer in the 'disturbed zone' of a deep geological disposal facility for radioactive wastes. I. Reaction of silicates with calcium hydroxide fluids. *Nirex Safety Series Report* **NSS/R244**. In preparation.

Savage, D. and Rochelle, C.A. (1993) Modelling reactions between cement pore fluids and rock: implications for porosity change. *Journal of Contaminant Hydrology* **13**: 365-378.

Sellier, A., Bournazel, J.P. and Mébarki, A. (1995) Une modélisation de la réaction alcalis-granulat intégrant une description des phénomènes aléatoires locaux. *Materials and Structures* **28**: 373-383.

Shayan, A., Diggins, R. and Ivanusec, I. (1996) Effectiveness of fly ash in preventing deleterious expansion due to alkali-aggregate reaction in normal and steam-cured concrete. *Cement and Concrete Research* **26**: 153-164.

Somerton, W.H. and Radke, C.J. (1983) Role of clays in the enhanced recovery of petroleum from some California sands. *Journal of Petroleum Technology, Society of Petroleum Engineers of AIME,* **March 1983**: 643-654.

Steefel, C.I. and Lichtner, P.C. (1994) Diffusion and reaction in rock matrix bordering a hyperalkaline fluid-filled fracture. *Geochimica et Cosmochimica Acta* **58**: 3595-3612.

Sydansk, R.D. (1982) Elevated temperature caustic/sandstone interaction: implications for improving oil recovery. *Society of Petroleum Engineers Journal* **August**: 453-462.

Thoenen, T. (1996) Potential alteration minerals formed by a hyperalkaline plume: status report. *Paul Scherrer Institut Report* **TM-44-96-10**.

Thomson, M.L. and Grattan-Bellew, P.E. (1993) Anatomy of a porphyroblastic schist: alkali-silica reactivity. *Engineering Geology* **35**: 81-91.

Thornton, S.D. (1988) Role of silicate and aluminate ions in the reaction of sodium hydroxide with reservoir minerals. *Society of Petroleum Engineers Reservoir Engineering,* **November 1988**: 1153-1160.

Tits, J. (1994) Immobilisation of radioelements by CSH phases: a literature survey. *Unpublished Nagra Internal Report.*

Valcke, E. and Cremers, A. (1995) Sorption of radionuclides by natural zeolites: a critical literature survey on the sorption properites of seven selected zeolites. *Unpublished Nagra Internal Report.*

Way, S.J. and Shayan, A. (1993) Synthesis and characterisation of crystalline analogues of alkali-aggregate reaction products. *Cement and Concrete Research* **23**: 471-479.

West, J.M., Coombs, P., Gardner, S.J. and Rochelle, C.A. (1995) The microbiology of the Maqarin site, Jordan - a natural analogue for cementitious radioactive waste repositories. In *Scientific Basis for Nuclear Waste Management Vol XIII,* M.R.S., 181-188.

Appendix I Tables summarising experimental studies of alkali-rock reaction

Table 1.1 Summary of radioactive waste experimental studies.

solid(s)	fluid(s)	T °C	duration (days)	type	flow rate m³ s⁻¹	analysis	results	author
albite; quartz; calcite; muscovite + quartz	Na-K-Ca-OH:Ca(OH)₂	70	146	column (30 cm)	2.8×10^{-10}	solids: SEM; EMPA; surface area, image analysis; model: finite difference coupled flow and chemistry (PRECIP)	fluids: concentration vs time data; solids: portlandite in calcite expt. CSH and CASH in remainder; model: reasonable agreement with expt, but scaling different (overestimation of reaction rate or surface area in model)	Bateman et al. (1995)
Clashach Sandstone	Ca(OH)₂ in 0.2 M NaCl	25	280	column (10 cm)	1.7×10^{-10}	fluids: pH, Na, K, Ca, Mg, Si, Al, S, Fe; solids: SEM/EDX; CEC; model: finite element coupled flow and chemistry (CHEQMATE)	fluids: concentration vs time data; solids: CSH/CASH precipitates; model: good reproduction of steady-state output pH; sorption of Ca on onto Fe-oxides invoked to interpret short-term behaviour	Braney et al. (1993)
Opalinus Clay	0.01-0.1 M NaOH	150, 175, 200	> 42	batch	-	fluids: pH, Na, Ca, Mg, Al, Si, Fe; solids: XRD, SEM, surface area; model: none	fluids: decrease in pH with time; decrease in steady-state pH with increasing temperature; solids: analcime, vermiculite, Na-rectorite products	Chermak (1992)
Opalinus Clay	0.008-0.08 M KOH	150, 175, 200	> 50	batch	-	fluids: pH, Na, Ca, Mg, Al, Si, Fe; solids: XRD, SEM, surface area; model: none	fluids: decrease in pH with time; decrease in steady-state pH with increasing temperature; solids: phillipsite, K-feldspar ± K-rectorite products	Chermak (1993)
Palfris Shale, Opalinus Clay	1.0 M NaOH (pH = 13.7), 1.0 M KOH (pH = 14.0)	75	> 365 (batch) > 54 (flow)	batch, flow-through with time	$5 - 7 \times 10^{-9}$	fluids: pH, Ca, Si, Al, Fe; solids: SEM/EDX, XRD, ATEM; model: none	fluids (batch): relatively constant pH, decreased Ca, increased Si and Al with time; solids: dissolution of calcite, ankerite, siderite, kaolinite and quartz; precipitation of tobermorite, albite, K-feldspar and K-zeolites	Chermak (1996)
cement-based wasteforms	deionised water	25	> 90	batch	-	fluids: Cs; solids: XRD, SEM/EDX	degree of partitioning of Cs into wasteform increased with increasing Si and Al content of cement. Pollucite and Cs-herschelite identified.	Hoyle & Grutzeck (1989)
cement	deionised water with CsCl, SrCl₂, CoCl₂	25	2	batch	-	fluids: Ca, Co, Cs, OH; solids: XRD, SEM, EMPA, SIMS, thermogravimetry	Co incorporated into cobalt oxychloride; Cs was retained in CSH and portlandite; Sr was retained in sulfoaluminates	Lameille et al. (1987)
marl, steel, cement, ion exchange resin	Na-SO₄-Cl; groundwater	25	1680	batch		fluids: not reported; solids: SEM, XRD, evolved gas analysis, LAMP, ATEM	steel - secondary iron oxyhydroxides, magnetite and hydroxysulphate 'green rust'; cement - removal of gypsum, precipitation of ettringite, CSH, CASH; marl - dissolution of calcite, dolomite, ankerite, quartz, feldspar, muscovite and illite-smectite; precipitation of saponite/corrensite/chlorite-smectite, CSH gel; Gallionella observed.	Milodowski et al. (1994)
Borrowdale Volcanic Group lithologies (crushed)	Na-K-Ca-OH	70	120	batch	-	fluids: pH, Na, K, Ca, Mg, Si, Ba, Sr, Mn, Fe, Al, Cl, ΣCO₂; solids: SEM, ATEM; model: reaction path software (EQ3/6)	fluids: concentrations vs time. Loss of Ca, K; gains of Al, Si, H⁺; gains highest for assemblages containing dolomite; solids: carbonates dissolved faster than silicates; secondary solids were CSH and Ca/Mg/Fe hydroxides. Possible precipitation of zeolites.	Rochelle et al. (1994b)
chlorite	NaOH/NaCl solutions of pH (25 °C) = 9.0, 10.3, 11.6, 13.0	25, 70	> 60	mixed-flow reactor	3.0×10^{-10}	fluids: Na, K, Ca, Mg, Si, Ba, Sr, Mn, Fe, Al, Li, B, SO₄, Cl, NO₃; solids: SEM/EDX	determination of dissolution rates and mechanisms. Non-stoichiometric (preferential) release of Al over Si at pH > 10.	Rochelle et al. (1994b, 1995a)
Borrowdale Volcanic Group lithologies (crushed)	'evolved near-field fluid': Na-Ca-K-OH-Cl-SO₄, pH = 10.7	70	> 120	batch	-	fluids: Na, K, Ca, Mg, Si, Ba, Sr, Mn, Fe, Al, Br, Cl, NO₃; solids: SEM/EDX, EMPA	fluid: decreases in pH, Ca; increases in Si, K, Mg. solids: precipitation of CSH.	Rochelle et al. (1994c)
Borrowdale Volcanic Group lithologies (disks)	'evolved near-field fluid': Na-Ca-K-OH-Cl-SO₄, pH = 10.7	70	> 120	batch	-	fluids: Na, K, Ca, Mg, Si, Ba, Sr, Mn, Fe, Al, Br, Cl, NO₃; solids: SEM/EDX, EMPA	fluid: decreases in Ca, SO₄; increases in Si. solids: precipitation of CSH, ettringite.	Rochelle et al. (1995b)
quartz, albite, K-feldspar, chlorite, biotite, muscovite, kaolinite, portlandite	Ca(OH)₂, pH = 12.5	25-100	> 67	batch, flow	9.0×10^{-11}	fluids: Na, K, Ca, Mg, Si, Ba, Sr, Mn, Fe, Al, B; solids: XRD, SEM/EDX, ATEM, infrared spectroscopy	portlandite solubility studies in temperature range 25-100 °C, pressure range 10-50 MPa. Reaction mechanism studies and rate determination (where possible) of other minerals at 70 °C. A variety of CSH, CASH solids identified as precipitates.	Savage et al. (1991); Savage et al. (1992b); Rochelle et al. (1992)

Table 1.1 (cont'd)   Summary of radioactive waste experimental studies.

solid(s)	fluid(s)	T °C	duration (days)	type	flow rate m³ s⁻¹	analysis	results	author
portlandite, quartz, albite, microcline, Ca-smectite, kaolinite, biotite, muscovite, chlorite	Na-K-Ca-OH, pH = 13.0	25-100	> 96	batch, flow	9.0×10^{-11}	fluids: Na, K, Ca, Mg, Si, Ba, Sr, Mn, Fe, Al, B solids: XRD, SEM/EDX, ATEM, infrared spectroscopy	portlandite solubility studies in temperature range 25-100 °C, pressure range 10-50 MPa. Reaction mechanism studies and rate determination (where possible) of other minerals at 70 °C. A variety of CSH, CASH solids identified as precipitates.	Savage et al (1992a); (1992b); Rochelle et al. (1992)

Table 1.2 Summary of cement and concrete industry experimental studies.

solid(s)	fluid(s)	T °C	duration (days)	type	flow rate m³ s⁻¹	analysis	results	author
orthoclase, microcline, albite, labradorite, anorthite, kaolinite, sericite, greywacke	Ca(OH)₂	22, 39	-> 730	batch	-	solids: XRD	CSH and/or hydrogarnet products for all minerals/rock except sericite.	van Aardt & Visser (1977)
opal, quartz	cement pore fluids	30	10	batch	-	solids: EMPA	Na, Ca and K ions migrate into opal aggregate during CSH formation.	Baker & Poole (1980)
quartz, chert, microcline, oligoclase, labradorite, hornblende, actinolite, augite, diopside, biotite, metabentonite, chlorite, serpentine, olivine, calcite, dolomite, siderite, gypsum, goethite, nepheline	1 M NaOH	23, 80	-> 265	batch	-	solids: SEM/EDAX. fluids: Si.	Relative reactivity of minerals established: high - chert, dolomite, siderite, gypsum; moderate - biotite, metabentonite; low - quartz, oligoclase, microcline, labradorite, augite, serpentine, chlorite, olivine, nepheline, hornblende, actinolite, diopside	Choquette et al. (1991)
albite, andesine, labradorite, anorthite, dacite, andesite, phonolite, basalt	concrete pore solutions	21	-> 360	batch	-	fluids: leaching with TET (tetramethylammonium-EDTA-TEA solution), then analysis for Ca, Sr, Si, Al, Fe, Mn, Mg, K and Na. solids: XRD.	Basalts (but not phonolites or dacites) release large amounts of alkalis to concrete pore solutions.	Goguel (1995)

Table 1.3 Summary of hydrocarbon industry experimental studies.

solid(s)	fluid(s)	T °C	duration (days)	type	flow rate m³ s⁻¹	analysis	results	author
Huntingdon Beach Sandstone, Wilmington Sandstone, amorphous silica, Ottawa Sand, montmorillonite, kaolinite, K-feldspar, biotite	0.1 M NaOH	52, 70, 74, 85	?	batch, column	?	fluids: Si, pH	Relative reactivity of minerals: amorphous silica > Ottawa sand > kaolinite > montmorillonite > K-feldspar > biotite. Sodium and hydroxide sorption on sandstones measured.	Bunge & Radke (1982)
kaolinite, quartz, muscovite, clinochlore, chamosite, Fontainebleau Sandstone	synthetic brine/cement chip mixture	90, 120	> 21	batch, columns (5 cm)	?	fluids: ICP-OES analysis - determinands not specified. solids: XRD, SEM/EDAX, ATEM.	CASH solids formed with increase in volume from single mineral experiments. Sandstone core suffered disaggregation.	Hughes et al. (1995)
Berea Sandstone	1 % NaCl + NaOH + SiO₂ (pH = 12.5)	90	> 60	column (30 cm)	10⁻¹⁰	fluids: Na, Si, pH	Confirmation of pseudo-first order kinetic model for silica release in hydrocarbon reservoirs.	Krumrine & Falcone (1988)
montmorillonite, kaolinite, illite, quartz	1 & 5 % NaOH + orthosilicate	82	> 60	batch	-	fluids: pH, Si, Na, Al. solids: XRD, SEM/EDAX, XPS.	Kaolinite was the most reactive mineral, quartz the least. Kaolinite reaction proceeds incongruently, with zeolites identified as products.	Mohnot et al. (1987)
Berea Sandstone	0.04 M NaOH + 0.06 M NaCl, 0.16 M NaCl	23	?	column	?	fluids: Na, pH. solids: CEC.	Ion exchange invoked to explain delay in breakthrough of OH⁻; slow dissolution reactions cause absolute differences in injected and produced OH⁻ concentrations.	Novosad & Novosad (1984)
Wilmington Sandstone	1 % NaCl + 1 % NaOH	52	?	column	?	fluids: pH, Si, Al. solids: SEM/EDAX, CEC, permeability	Ion exchange delays breakthrough of OH⁻; OH⁻ concentration eventually reaches a value slightly less than that injected. Hence for longer cores and lower flow rates, more OH⁻ consumption is predicted. Kinetics important for describing total alkalinity loss.	Somerton & Radke (1983)
Various sandstones	4 % NaOH	85	?	column (8 cm)	?	fluids: pH, Si, Al. solids: SEM	Clay and large surface area, silica minerals were the most reactive. There was a porosity increase and weight loss of all sandstones studied. Permeabilities increased in some samples and decreased in others. Zeolites (phillipsite) were identified as precipitates.	Sydansk (1982)
quartz, albite, microcline, muscovite, biotite, kaolinite, montmorillonite, chlorite	0.12-1.0 M NaOH for batch expts.; 2.9 % NaCl + 2 % NaOH for columns	24, 70	> 60	batch, column	?	fluids: pH, Na, Si, Al	Biotite and chlorite were relatively unreactive at both temperatures. At 24 °C, reactivity for other minerals was: muscovite > microcline > albite > quartz. At 70 °C, the order was: quartz > microcline > albite > muscovite. Precipitation of zeolites inferred from experimental data for kaolinite dissolution. Column tests with kaolinite failed to achieve the amount of OH⁻ consumption predicted from the results of the batch experiments.	Thornton (1988)

Table 1.4 Summary of 'other' experimental studies.

solid(s)	fluid(s)	T °C	duration (days)	type	flow rate m³ s⁻¹	analysis	results	author
opal, chert, quartz, oligoclase, labradorite, microcline, nepheline, calcite, dolomite, gypsum, biotite, chlorite, illite, metabentonite, hornblende, actinolite, diopside, augite, olivine, serpentine, pyrite, goethite, limestone	$Ca(OH)_2$	23, 80	-> 265	batch	-	fluids: Na, K, Mg, Si, Al solids: XRD, SEM, infrared spectroscopy model: reaction path simulations (PHREEQE)	Relative reactivity of minerals was established as follows (at 80 °C): highly reactive - opal, chert, metabentonite, nepheline, dolomite reactive - oligoclase, quartz poorly reactive - labradorite, microcline, biotite, calcite unreactive - chlorite, gypsum, hornblende, actinolite, diopside, augite, serpentine, olivine, pyrite, goethite. CSH and CASH phases were identified as products. The order of reactivity established experimentally is similar to that observed using computer simulations.	Bérubé et al. (1990)
montmorillonite, metabentonite, illite, kaolinite, halloysite	2.8 M NaOH	25	10	batch	-	fluids: Si, Al, Ca, Mg, Na, K solids: XRD	Order of reactivity was: kaolinite > halloysite > montmorillonite > metabentonite > illite. NaOH treatment of halloysite extensively dissolved its aluminosilicate framework. Precipitates were not identified.	Carroll & Starkey (1971)
Wyoming and Kinney bentonites	0, 0.1, 0.5, 1.0, 3.0 M Na/KOH	35, 60	-> 270	batch	-	solids: XRD, ATEM	Both bentonites reacted to form randomly interstratified illite-smectite. Illite-smectite is much less expandable than smectite.	Eberl et al. (1993)
palygorskite, sepiolite	0.001-0.008 M NaOH	150	1	batch	-	solids: XRD	Palygorskite was converted to smectite in 0.001 M NaOH. Analcime + smectite formed when NaOH > 0.003 M NaOH. Sepiolite was destroyed at concentrations > 0.006 M NaOH.	Golden et al. (1985)
kaolinite, kaolinite-bentonite, Mg-montmorillonite	NaOH, pH = 9, 11, 13	25	-> 30	column	?	solids: permeability, XRD	Permeability decreased for all solids at pH = 13. This decrease is attributed to the precipitation of calcite in the kaolinite and kaolinite-bentonite samples and brucite in the Mg-montmorillonite sample.	Lentz et al. (1985)