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A review of analogues of alkaline alteration with regard to long-term barrier performance

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ABSTRACT

Cement and concrete will be used as fracture grouts, shotcrete, tunnel and borehole seals, and as matrices for waste encapsulation *inter alia* in geological repositories for radioactive wastes. Alteration of the host rock and/or swelling clay in waste package buffers and tunnel backfills by hyperalkaline solutions from cement/concrete may be deleterious to system performance through changes in the physicochemical properties of these barrier materials.

Analogue systems (and timescales) relevant to the understanding of the alkaline disturbed zone include: industrial analogues, such as alkaline flooding of hydrocarbon reservoirs (up to 30 y), cement-aggregate reactions (up to 100 y) and the Tournemire tunnel (up to 125 y); and natural analogues, including the hyperalkaline springs at Maqarin, Jordan (more than 100,000 y), saline, alkaline lakes (more than 1,000,000 y) and certain fracture fillings in granites (more than 1,000,000 y).

These systems show that alkaline alteration can be observed for thousands of years over distance scales of hundreds of metres under extreme conditions of hydraulic gradients in fractured rocks (Maqarin), but may be limited to a few centimetres over tens to a hundred years in mudstone (Tournemire). Important reaction mechanisms for retardation of alkaline fluids include: fluid mixing (alkaline oil floods, Maqarin), ion exchange (alkaline oil floods, Tournemire) and kinetic mineral dissolution-precipitation reactions (all systems studied). Qualitative and quantitative kinetic data for mineral reactions are available from cement aggregate reactions and the Searles Lake analogue, respectively. Short-term alteration observed in cement-aggregates is characterized by calcium silicate hydrate (C-S-H) minerals and incipient zeolite formation, whereas evidence from the Tournemire tunnel shows the growth of K-feldspar after relatively short time intervals (tens to a hundred years). There is a tendency for alkaline alteration to result in porosity decreases, but locally, porosity may be enhanced (e.g. near-injection well interactions in alkaline oil floods, or at fracture margins at Maqarin, Jordan). Data from industrial and natural analogues may thus supply some key data for bridging time and space scales between laboratory and *in situ* experiments on one hand and the requirements for safety assessment on the other.

KEYWORDS: analogue systems, waste encapsulation, alkaline alteration, barrier performance, hydraulic gradients, Maqarin, Jordan, Tournemire, France.

Introduction

CEMENT and concrete will be used as fracture grouts, shotcrete, tunnel and borehole seals, and as matrices for waste encapsulation *inter alia* in geological disposal facilities for radioactive wastes (e.g. SKB, 2006; Gribi *et al.*, 2008). Alteration of the host rock and/or swelling clay in waste package buffers and tunnel backfills by

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alkaline solutions from cement/concrete may be deleterious to system performance through changes in the physical and chemical properties of these barrier materials (Savage, 1997). The scientific and technological emphasis to characterize these issues has been placed mainly upon laboratory studies (e.g. Savage *et al*., 1992; Bauer and Berger, 1998; Michau, 2005; Fernández *et al*., 2010) which have then supplied input data for predictive coupled modelling to address greater time and distance scales (e.g. Haworth *et al*., 1988; De Windt *et al*., 2004; Montori *et al*., 2008). In the last ten years, efforts have also been made to use underground *in situ* experiments as a means to extend distance scales beyond those encountered in the laboratory (e.g. Soler *et al*., 2004, 2006). Unfortunately, the process of upscaling is not straightforward, especially concerning topics such as: long-term reaction mechanisms; reactive surface area of mineral dissolution and growth; the nature and types of secondary mineral formation; and the coupling of porosity and permeability.

Although less well constrained than laboratory data, information from analogue systems has the potential to increase confidence in using laboratory and *in situ* data to extrapolate to greater time and distance scales. In general, the use of data from analogues in predictive modelling has not occurred, principally due to the conservative nature of many system assessments and a perceived lack of suitable data (e.g. Smith *et al*., 2008; Gribi *et al*., 2008). To a certain extent, this situation has pertained because alteration under hyperalkaline conditions in the natural environment is rare, and moreover, alteration under mildly alkaline conditions has been deemed of little relevance. However, the latter can provide evidence for the likely magnitude and rate of alteration where the use of low-pH cements (e.g. Savage and Benbow, 2007) is envisaged, or where Ordinary Portland Cement (OPC) pore fluids have undergone partial reaction with geological materials (e.g. Savage *et al*., 2010). Trace element and microbiological behaviour has been investigated in mildly alkaline springs at the Oman ophiolite complex (McKinley *et al*., 1988) and preliminary results from studies of alkaline alteration (pH 9−11) of bentonite in ophiolite complexes in the Troodos Mountains of Cyprus and in the Philippines have also been reported (McKinley *et al*., 2008; Milodowski *et al*., 2009).

Groundwater that has reacted with cement will migrate and potentially react chemically with the enveloping rock and groundwater. Alteration can be viewed as consisting of two main components (Fig. 1): (1) a zone closest to the cement/concrete where there may be mineral alteration. The principal reactions will be the dissolution of rock-forming minerals and the precipitation of secondary solid reaction products. These solids may be amorphous or crystalline or both. Some modification of the physical properties of the rock/clay buffer (porosity, permeability) may occur as a result of alkaline alteration. (2) A zone further from the cement/concrete where pH is still elevated from its unperturbed value, but lower than that in the zone of mineral alteration. In this zone, ion exchange is important, and mineral alteration reactions occur at a much slower rate so that physical-property changes are

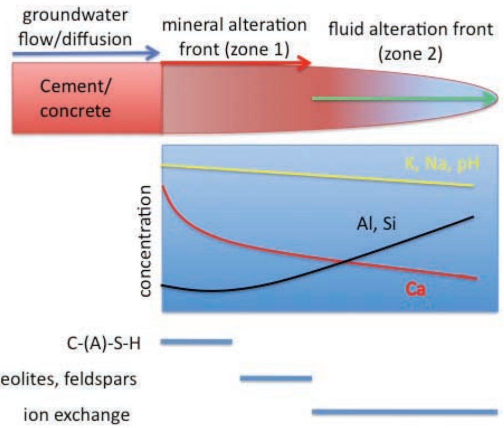

FIG. 1. Schematic diagram of the migration and reaction of hyperalkaline fluids with rocks and clay barriers, showing possible variations in fluid composition and alteration mineralogy (after Savage, 1998). A zone of perturbed fluid composition (elevated pH, Na, K, Al and Si) where ion exchange reactions dominate ('Zone 2'), migrates ahead of a zone of mineral dissolution and growth ('Zone 1'). Calcium concentrations in the migrating cement pore fluid decrease relatively close to the cement/concrete due to precipitation in C-(A)-S-H solids through reaction with the host rock. Similarly, Al and Si concentrations in the migrating fluid increase with distance due to dissolution of host rock/buffer minerals. Secondary minerals which form as a result of these interactions reflect the composition of the fluid, such that calcium silicate hydrates (C-(A)-S-H) form nearest the cement, whilst zeolites and feldspars form further away. With time, this mineral sequence evolves as the fluid migrates.

less likely to occur. The elevated pH will have an impact on processes such as ion exchange, sorption of radionuclides, clay swelling pressure, the activity of microbes and the mobility of colloids. A schematic view of the nature of alkaline alteration and the migration of hyperalkaline fluid is shown in Fig. 1.

A key issue here in predicting the magnitude of any alteration over long timescales is the problem of up-scaling data from laboratory and *in situ* experiments to the time and distance scales of relevance to performance assessment (Fig. 2). This paper reviews evidence from industrial and natural analogues relevant to assessing this problem. Data from archaeological analogues have been excluded from this review, but other authors have summarized this evidence elsewhere (e.g. Miller *et al*., 2000). Issues relating to radioelement solubility/sorption, colloid stability and viability of bacteria have also been excluded from this review.

Analogue systems

Analogue systems are here divided into those that can be classified as *industrial* or *natural*. Industrial analogues, including cement-aggregate reactions and alkaline flooding of hydrocarbon reservoirs, serve to partially bridge the gap in time and space scales between laboratory and *in situ* tests on the one hand and natural analogues on the other. Time-scales are up to a hundred years or so and space-scales up to hundreds of metres. Although time scales are much reduced compared to those of relevant natural systems, boundary conditions are generally better defined and also include real cements of some description. Natural analogues cover much larger time and distance scales and would include systems such as Maqarin, Jordan and saline, alkaline lakes.

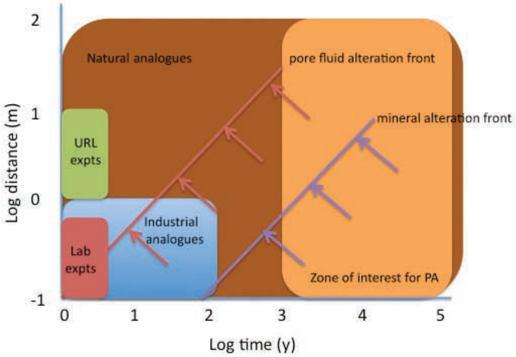

FIG. 2. Schematic illustration of the differing space and temporal scales associated with different data sources and those required for performance assessment (PA). The positions of the pore fluid and mineral fronts are schematic and their locations will be a function of site-specific groundwater flow/diffusion.

Industrial analogues

Cement aggregates

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 cracking (both internal and surficial), exudation of viscous gels, discolouration, or any combination of the three. These reactions have been studied extensively by researchers in the cement and concrete industry and provide analogous evidence for mineral-alkali reactions over the timescale of tens to a hundred years over relatively short spatial scales (~1 cm). Data are available for mineralogical reaction sequences, but not for fluid chemistry. Three conditions must be satisfied to sustain alkali-aggregate reactions in concrete (Bérube *et al*., 2002): (1) the presence of reactive aggregates; (2) a high alkali concentration in the cement pore solution; (3) exposure to high humidity.

Alkaline flooding of hydrocarbon reservoirs

Alkaline fluids 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 a decrease in pH of the system. The spatial extent of such interactions is of the order of 100 m, whereas flood operations are of the order of months to years, and reservoir lifetimes are of the order of tens of years. Injected fluids are NaOH/KOH-type (pH 12–13), usually with no introduced calcium. Surfactants (scaling inhibitors) may also be introduced with alkaline fluids to try to minimize scaling problems. During alkaline floods, the flow rates of injected fluids (m^3/day) and rock porosities (tens of percent) are high in comparison with likely repository environments so that dominant processes are water mixing and ion exchange, although mineral dissolution and precipitation also contribute to longer-term alkali loss.

The Tournemire tunnel, southwest France

To study the interaction of mudstones with cementitious materials, the Institute for Radioprotection and Nuclear Safety (IRSN) and the Scientific Research National Centre (CNRS) in France have developed a research programme in the so-called 'Tournemire Experimental Platform'. This programme, integrated in the TRASSE (Transferts des RAdionucléides dans le Sol, le Sous-sol et vers les Ecosystèmes) Research Group, aims to describe the modifications of Jurassic mudrocks in contact with cementitious materials over various time scales (from a few years to a hundred years). The Tournemire experimental platform is based on a tunnel built between 1882 and 1886 and several galleries excavated since 2003 through Jurassic marls and mudstones in southwest France. Mudstones are 250 m thick, sandwiched between two calcareous aquifers, the Aalenian (30 m thick) and the lower Carixien (50 m thick). The mudstone comprises silicates (clays, quartz, feldspars and micas totalling 86%), sulphides (pyrite = 3%), carbonates (calcite, dolomite = 10%) and organics (1%) (Tinseau *et al*., 2006). In the 1990s, exploration boreholes were drilled from the basement of the tunnel and then filled with concrete and cement that have been in contact with the mudstones for 15−20 y. In 2003, two experimental research galleries were excavated perpendicular to the tunnel and covered by several centimetres of four concrete formulations. The field-based studies are complemented by laboratory experiments and modelling of cement-rock reactions. The type of concretes at Tournemire varies according to location: the tunnel masonry (made of breeze blocks in limestone) is bedded with lime, and is siliceous (its initial chemical composition is not known), whereas the various borehole cores are of CEM II 32.5 concrete (ISO 9002), which is composed of cement, gypsum and calcium carbonate.

Natural analogues

Maqarin, Jordan

The pyrometamorphic rocks and associated hyperalkaline groundwater plumes of the Maqarin site have been investigated by various radioactive waste management agencies as analogues of cement-based repositories since 1989. The work has been conducted in a number of phases and summary descriptions can be found in Smellie *et al*. (2001) and Baker *et al*. (2002). The site is located on the south side of the Yarmouk valley in northwest Jordan and lies on the border with Syria, ~16 km north of the city of Irbid and 25 km east of the River Jordan[1]. The hyperalkaline groundwaters in the area are the product of leaching of pyrometamorphic rocks produced by high-temperature, low-pressure metamorphism of highly bituminous siliceous limestones (Alexander, 1992; Linklater, 1998; Smellie, 1998). The period of metamorphism is uncertain; geomorphological considerations suggest a date of ~600 ka, and not earlier than 150 ka. The alkaline groundwaters emanating from the 'Cement Zone' rocks flow through fractures in the adjacent enclosing unmetamorphosed sedimentary strata (comprising bituminous clay, biomicrite and chalk), to discharge through wadi colluvium and gravels in a series of springs along the floor of the Yarmouk valley. Fractures conducting alkaline groundwaters are intercepted above the valley floor in a disused railway cutting (Maqarin Station) and in a dam site exploration adit in the eastern part of the area. Extensive deposits of travertine are formed at the spring discharge points as the $Ca(OH)_2$-saturated groundwaters interact with atmospheric CO_2. Compared with likely repository environments, Maqarin is relatively well fractured and subject to high hydraulic gradients. Moreover, the host rock is a clayey limestone, rather than a true mudstone. Reactivation of fractures, triggered by landslip activity associated with the instability of the very high relief sides of the Yarmouk river may account for the periodic sealing and reactivation of fracture pathways indicated from mineralogical studies.

Saline, alkaline lakes

Saline, alkaline lakes provide relevant natural system evidence for the alteration of mudstones and volcanic tuffs by mildly alkaline fluids. Although pH in these systems is less than that measured in pore fluids in OPC cements (pH 7.5−10.5) (Surdam and Sheppard, 1977; Taylor and Surdam, 1981) and carbonate contents are greater, their compositions are similar to low-pH cement pore fluids and OPC cement pore fluids partially reacted with rocks (e.g. Chermak, 1992; Chermak, 1993), and are thus analogous to that

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[1] Note that the site is now flooded by a water-supply reservoir.

part of the system where partial reaction and mixing of cement pore fluids with ambient groundwater has taken place. Evidence from these systems can help define which alteration minerals are stable in the long-term during the reaction of rocks with alkaline fluids, for input to predictive computer models.

Fracture fills in granite

The solid products of the interaction of groundwater with granitic rocks can include a wide range of minerals, such as clays, oxides, carbonates, feldspars and zeolites, depending upon groundwater composition, host rock type and geological history. In some instances, water-rock reactions at temperatures greater than ambient (50–150ºC) can produce rock alteration sequences similar to those hypothesized for cement–rock reactions at 25ºC. For example, laumontite and analcime (a Ca-zeolite and Na-feldspathoid hypothesized to form during cement–rock interactions) can occur with clay, quartz and calcite as a fracture-filling in granite (e.g. Sandström *et al*., 2009). Mineral textural information from such fracture fills regarding how laumontite may replace analcime and *vice versa* can thus inform modelling choices regarding potential porosity changes involving these minerals during cement-rock reactions.

Issues relevant to long-term barrier performance

The following issues are important with regard to the assessment of the impacts of any alteration: physical and temporal scale; titration/reaction mechanisms; kinetics; secondary minerals and mineral sequences; and porosity-permeability modifications.

These issues are discussed below along with evidence from analogues relevant to them.

Time and space scales

The potential impact of alkaline alteration upon repository performance is largely dependent upon its spatial and temporal scales (Savage, 1997; Baker *et al*., 2002). In turn, the scale and extent are dependent upon factors such as: the nature and magnitude of groundwater transport; the structure and mineralogical composition of the host rock; the chemical composition of ambient groundwater; and the precise rate and nature of the coupled reactions accompanying hyperalkaline fluid migration. The temporal and physical scales are also controlled to a large degree by the mass of cement and its distribution in the repository, i.e. whether concentrated in large masses of backfill or tunnel plugs, or in a more diffuse distribution as fracture grouts.

Analogue evidence

Observations from cement-aggregate systems demonstrate that reactions are limited in space (centimetre-scale), due to a finite amount of reactive hydroxyl ions. The spatial extent of alkaline flooding operations in oil reservoirs is in the order of a hundred metres, but pressure gradients are much higher than would be expected in a repository environment. Alkaline flood operations are in the order of months, and reservoir lifetimes are in the order of tens of years. At Tournemire, a 1.5 cm-thick zone in mudstone adjacent to 15 year-old concrete in a borehole is defined by precipitates of solid carbonates (calcite, vaterite, aragonite), ettringite and C-S-H gel, whereas further away (5–10 cm), a *texturally* unperturbed zone shows K-feldspar overgrowths and calcite and gypsum precipitates (Tinseau *et al*., 2006). The evidence from Tournemire shows that a zone of ion exchange can advance in front of a zone of mineralogical alteration (Fig. 1).

Observations from the Eastern Springs area of Maqarin indicate that the alkaline plume can extend for at least 500 m from its source in the Cement Zone (Alexander and Mazurek, 1995). However, the Maqarin site is highly fractured and relatively transmissive with high hydraulic gradients, so that development of the high pH plume is certainly much more extensive than it would be in a real repository situation.

Reaction mechanisms

Zones of pore fluid perturbation and rock alteration develop around masses of cement/concrete in response to chemical reactions which titrate hydroxyl ions in migrating cement pore fluids. The mechanisms of hydroxyl ion titration can be envisaged to consist principally of: dilution and groundwater mixing; ion exchange (including surface complexation); mineral hydrolysis; and mineral growth. The last process ‘locks up’ irreversibly hydroxyl ions, whereas the others are reversible reactions.

Mixing of cement pore fluids with ambient groundwater or pore fluids in the rock mass will cause a decrease in pH of the mixed fluid through simple dilution effects and by chemical reaction. Reactions with carbonate and bicarbonate may decrease pH as follows:

$$HCO_3^- + OH^- \rightarrow H_2O + CO_3^{2-} \qquad (1)$$

Reactions of this type are especially important in sedimentary host rocks due to higher ambient values of PCO_2 than in fractured hard rocks (Coudrain-Ribstein *et al.*, 1998), but groundwaters in some of the latter rock types may also be saturated with calcite (e.g. in the Borrowdale Volcanic Group at Sellafield; Bath *et al.*, 1996). Differences in PCO_2 between cement/concrete and sedimentary formations such as mudstone can lead to the development of solid carbonates at the interface between the two materials (e.g. as demonstrated at the Tournemire analogue; Tinseau *et al.*, 2006).

Ion exchange reactions will principally occur with layer silicates according to equilibria such as:

$$\text{Mineral-H} + Na^+ + OH^- \rightleftharpoons \text{mineral-Na} + H_2O \qquad (2)$$

Such reactions may be regarded as fast (instantaneous) and depend upon the rate of contact of the fluid with the clay particles. In addition to titration of hydroxyl ions, consideration must be given to potential changes in physicochemical properties of clays due to the replacement of sodium by calcium ions. For example, replacement of sodium in montmorillonite by calcium will lead to a decrease in swelling pressure in bentonite. Clays may also participate in protolysis reactions at edge sites which can be significant in retarding OH^- (Bradbury and Baeyens, 2003). Exchange reactions are more important in clays than fractured hard rocks, but the latter may contain micas, or clays in fracture fills that may participate in such reactions.

Mineral hydrolysis reactions can also contribute to retardation of OH^- ions at elevated pH, due principally to changes in pH-dependent aqueous speciation of Al and Si. For example at pH <10, albite (feldspar) hydrolysis can be described by:

$$NaAlSi_3O_8 + 4H^+ \rightarrow Na^+ + Al^{3+} + 3SiO_{2(aq)} + 2H_2O \qquad (3)$$

Whereas at 10 < pH < 13:

$$NaAlSi_3O_8 + 3OH^- + 2H_2O \rightarrow Na^+ + Al(OH)_4^- + 3HSiO_3^- \qquad (4)$$

and at pH >13:

$$NaAlSi_3O_8 + 6OH^- + 2H_2O \rightarrow Na^+ + Al(OH)_4^- + 3H_2SiO_4^{2-} \qquad (5)$$

Thus mineral dissolution at a pH above 10 can consume OH^- in contrast to the reaction encountered at the usual ambient pH in groundwater and may remove OH^- from solution if coupled with secondary mineral precipitation (see below). However, these reactions are slow and thus demand a kinetic description in coupled modelling.

The precipitation of secondary minerals may contribute to the consumption or generation of OH^-, according to pH and reaction stoichiometry (see Savage *et al.*, 2007). Although growth of C-S-H solids is generally fast and observable over laboratory experimental timescales, that of aluminosilicates is generally much slower and restricted to analogue occurrences at ambient temperature. Since mineral growth can perturb rock/barrier porosity and permeability, the precise rate and mechanism are key issues in up-scaling short-term experimental data.

Analogue evidence

The reaction mechanisms for alkali-aggregate reaction in concrete have been described both in generic terms (Bérubé and Fournier, 1986; Gillot, 1995; Way and Shayan, 1993; Brouxel, 1993) as well as for specific solids (e.g. Goguel, 1995). Although reaction is dominated by the formation of a sodium silicate gel, at a late stage of gel formation, Ca enters the gel in large amounts and this is believed to halt the gel-formation process. The reaction is widely assumed to be diffusion-controlled (French, 1980). Formation of these gels can generate pressures in the order of several MPa (French, 1980). A feature of some alkali-aggregate reactions in concretes 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 minerals in the rock. In a repository context, reaction of minerals such as feldspars has the potential to extend the migration of the alkaline plume and increase the pH of migrating pore fluids. Release of Na/K from rocks has been identified for basalts (Batic *et al.*, 1994; Goguel, 1995), impure limestones (Grattan-Bellew, 1995) and dolomite (Poole and Sotiropoulos, 1980).

Some alkaline flooding studies of oil reservoirs emphasize mineral (principally clay) ion exchange reactions as the only process by which alkali is consumed in sandstone reservoirs (e.g.

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) and hence responsible for the spatial extent of alkaline conditions. However, Bryant *et al*. (1986) emphasized the need to address both ion exchange and mineral dissolution-precipitation reactions to model alkali migration quantitatively so that the spatial extent of alteration could be predicted. Bunge and Radke (1982) were the first to recognize that (reversible) ion exchange was responsible for the delay in arrival of the alkali pulse during alkali flooding (with the lower the pH of the injected fluid, the longer the delay) whereas kinetically-controlled (irreversible) mineral dissolution-precipitation reactions caused the overall depletion of OH^-, and hence decrease in pH in injected fluids. They attributed the slow reaction to the dissolution of quartz, rather than clay minerals, which they observed to be much slower than the former.

Modelling of the cement-mudstone interactions in the Tournemire tunnel has necessitated the incorporation of kinetic descriptions of mineral dissolution and growth; an equilibrium assumption failed to reproduce observed mineral distributions (De Windt *et al*., 2008).

Alteration mineral sequences and inferred reaction mechanisms at Maqarin confirm hypothetical alteration patterns suggested by Savage (1997, 1998) according to Alexander and Mazurek (1995). Reaction-path modelling of alteration adjacent to fractures at Maqarin highlighted the sensitivity of alteration patterns to the assumed rate of growth of secondary minerals (Steefel and Lichtner, 1998). When rate constants for secondary mineral growth were the same in both fracture and bulk rock, the matrix became cemented before the fracture, resulting in downstream migration of the hyperalkaline plume. If rates were as little as one order of magnitude greater in the fracture than in the matrix, then the fracture sealed first, causing alteration to cease due to reduction in fracture permeability (Steefel and Lichtner, 1998).

At the Searles Lake analogue, modelling of sediment accumulation, compaction and diagenetic reaction in the pH range 9–10 has shown that the zonal pattern of clay alteration can be reproduced using published kinetic and thermodynamic data for smectite dissolution (Savage *et al*., 2010). Growth of secondary minerals such as illite, Mg-montmorillonite, analcime and K-feldspar was modelled with rates estimated using mineralogical data from the Searles Lake drill core. Alternative models for the kinetics of montmorillonite dissolution published by Cama *et al*. (2000) and Sato *et al*. (2004) produced differing results, with the Cama transition state theory (TST) model dissolving the smallest amount of clay and, moreover, producing a pattern of dissolution and precipitation of secondary minerals most similar to the natural system. However, clay dissolution was equally sensitive to the assumed rates of growth of secondary minerals. Moreover, it is clear from the results that any model to describe clay alteration at Searles Lake necessitates the inclusion of clay hydrolysis reactions to reproduce the observed patterns of mineral distribution. This assessment provides a test of the accuracy and reliability of published data in the application of models of smectite dissolution in the long-term and demonstrates that smectite will be reactive under mildly alkaline conditions under conditions of advective fluid transport.

Kinetics

The dissolution and precipitation reactions of aluminosilicate minerals (the principal components of repository host rocks) will be relatively slow (compared with ion exchange) so that a description of the rates of such processes is necessary to predict the detail of mineral sequences and porosity-permeability changes over relevant distance scales (e.g. Knapp, 1989; Marty *et al*., 2009).

A general rate equation for mineral dissolution is as follows (e.g. Lasaga, 1998):

$$\text{Rate} = A\text{k}_0(a_{\text{H}^+})^p(\Omega - 1) \qquad (6)$$

where $\Omega = IAP/\text{K}_{\text{eq}}$, k_0 is the rate constant for dissolution or growth at pH = 0, A is the reactive surface area, IAP is the ion activity product, K_{eq} is the equilibrium constant and p is the (often fractional) dependence of rate upon the activity of H^+ (or in this case more relevantly, the activity of OH^-). Aluminosilicate minerals show increasing rate with increasing pH due to changes in surface charge with pH such that deprotonation of silanol sites occurs at pH >8, leading to breaking of bonds and dissolution of the aluminosilicate framework.

The concept of reactive surface area is fundamental to modelling any geochemical system. The often-observed difference in rates of aluminosilicate dissolution between field and laboratory systems has led some authors to suggest that A may be different between feldspars present in weathered granites and those in laboratory experiments, leading to a difference of rate of 2–3 orders of magnitude between those measured in the field as compared with those measured in the laboratory (e.g. White and Brantley, 1995; 2003). However, more recent interpretations have suggested that this discrepancy may be more attributable to the estimation of departure from equilibrium in the coexisting pore fluid as a result of assumptions regarding the rate of growth of solid weathering products (e.g. Maher *et al*., 2009). Nevertheless, recent modelling exercises (e.g. Hoch *et al*., 2004; Michau, 2005; Soler *et al*., 2006) have highlighted the difficulties of the *a priori* application of surface-area data to fit the results of laboratory and *in situ* tests. Differences in rate can also be related to the differences in the nature of reacting surfaces. Greater densities of defects and discontinuities can result in faster dissolution than more perfect crystals because their effective surface area is greater (e.g. Schott *et al*., 1989). In crushed experimental mineral charges, there will be a greater proportion of more reactive crystal edge, corner and defect sites than on a planar natural fracture surface or rock joint face undergoing weathering or reaction.

Most modellers assume that equation 6 is equally applicable to modelling mineral growth as well as dissolution (with a reversal of sign), but this is probably unrealistic. Again, the critical issue is the reactive surface area (A), and especially how it may change with time. Typically in reaction-transport modelling, A is kept constant with time. However, for a secondary mineral, surface area is initially created by nucleation and is subsequently modified by crystal growth and dissolution and by crystal ripening. Nucleation is an extremely important process to consider, since at supersaturation levels above a critical value, its rate may be very large, and therefore it may control the rate at which surface area is generated. In addition, the process of Ostwald ripening, whereby smaller crystals with higher solubility dissolve and reprecipitate as larger crystals is important to include in the analysis as ripening counteracts rapid surface area generation by nucleation. Although theoretical approaches to model such processes exist (e.g. Steefel and Van Cappellen, 1990; Fritz *et al*., 2009), they have not been applied extensively due to a lack of relevant data for mineral-fluid interfacial free energies *inter alia*. However, it has been recognized that the interaction of cement pore fluids with rocks and other engineered barrier components may well develop through an Ostwald step type sequence of alteration (e.g. Savage *et al*., 2007) which will demand greater consideration of such processes in future modelling studies.

Evidence from analogues

Qualitative evidence from cement–aggregate reactions demonstrates that some rock types may react rapidly (generally fine-grained volcanic rocks, sedimentary rocks containing amorphous silica, dolomites) and others more slowly (granites, metamorphic rocks) (e.g. Ponce and Batic, 2006).

De Windt *et al*. (2008) modelled the evolution of alkaline alteration fronts at Tournemire utilizing published laboratory data for mineral dissolution kinetics and noted the sensitivity of the growth of zeolites to the assumed rate constants. Although a better match was obtained using an assumption of rate-controlled processes (as compared with an equilibrium assumption), the modelling predicted muscovite and zeolites, rather than K-feldspar as the principal neoformed mineral, which may have been due to assumed reactive surface areas for these precipitates.

Age relationships of sediment deposition in saline, alkaline lakes show that the zeolites can form on the timescale of a few hundred years and complete conversion of tuffs to zeolites (zeolitization) can occur over a few thousand years (Hay, 1964). These observations demonstrate that zeolitic alteration, although generally absent from short-term laboratory experiments, can take place over timescales relevant to radioactive waste safety assessment.

Savage *et al*. (2010) tested the applicability of three different models for the dissolution of montmorillonite to describe the diagenesis of clay minerals under mildly alkaline conditions ($9 < \mathrm{pH} < 10$) at Searles Lake, California. This involved two transition state theory (TST) type models (Cama *et al*., 2000; Sato *et al*., 2004) and an empirical model based upon the dependence of rate upon silica concentration in the fluid (Cama *et al*., 2000). Savage *et al*. (2010) noted that the diagenetic history of the Searles Lake sediments was best reproduced using the TST model of Cama *et al*. (2000).

Regarding secondary mineral growth rates, Savage *et al*. (2010) estimated data from the

Searles Lake analogue using information for crystal grain sizes and sediment ages published by Hay and Guldman (1987), using an expression that describes mineral particle size as a function of time (Lasaga, 1984) which assumes a linear crystal growth mechanism:

$$r = r^0 + k_+\bar{V} \qquad (7)$$

where r^0 is the initial particle diameter at $t = 0$ (here assumed to be zero); k_+ is the growth rate constant (mol m^{-2} s^{-1}), $\bar{V}$ is the mineral molar volume (m^3 mol^{-1}). Adoption of these rates in the computer simulations carried out by Savage *et al.* (2010) required slight modifications to reproduce the diagenetic mineral sequences at Searles Lake (Table 1).

Secondary Minerals

The role of secondary minerals in governing the potential alteration of rocks and engineered barrier system (EBS) components by hyperalkaline fluids has been reviewed recently (e.g. Gaucher and Blanc, 2006; Savage *et al*., 2007) and is principally through the influence on solution chemistry (notably pH) and the associated effects on the rate and mechanism, and departure from equilibrium of mineral dissolution (e.g. Oda *et al*., 2004; Vieillard *et al*., 2004), together with changes to porosity which affect mass transport.

Analogue evidence

Evidence for secondary mineral formation from cement–aggregate reactions in concretes of variable age is summarized in Table 2. Reaction products generally take the form of thin (<1 mm) reaction rims of alkali-silica gel around aggregate particles, some of which with time crystallize to a calcium silicate hydrate mineral such as okenite ($CaSi_2O_4(OH)_2.H_2O$), or a zeolite, such as erionite or both. Silica, in all its forms, is identified as being the principal reactant. Dolomite is subject to so-called de-dolomitization reactions which involve the replacement of dolomite by calcite and brucite (Poole and Sotiropoulos, 1980):

$$CaMg(CO_3)_2 + 2NaOH \rightarrow CaCO_3 + Mg(OH)_2 + Na_2CO_3 \qquad (8)$$

At the Tournemire tunnel site, Tinseau *et al.* (2006) observed that in the absence of water, no significant modification of the host mudrock was observed, even after 125 years, except for pyrite dissolution and gypsum precipitation. In the presence of water, growth of gypsum, mixed-layer clays, zeolites and K-feldspar was observed. This was enhanced with time, flow rate and the nature of the concrete. Wet, 125 year-old contacts between mudrock and cement showed dissolution of clay, quartz and dolomite, with precipitation of calcite, gypsum, Na-zeolites and K-feldspar (the latter two as overgrowths). The growth of a few Na-zeolites was also observed through SEM observations (unconfirmed by XRD) in samples from the upper part of 15-year-old borehole samples (at around 1.1 m under the tunnel) (Tinseau *et al*., 2008). Quartz also decreased significantly in the first millimetres of mudstone in contact with the concrete. The zone of pronounced mineral growth at Tournemire is 1.5 cm thick, with ettringite and calcite forming, whereas further away (5−10 cm), a texturally unperturbed zone shows K-feldspar overgrowths,

TABLE 1. Estimated and modified growth-rate constants for analcime, clinoptilolite, K-feldspar and phillipsite from the Searles Lake analogue (at 60ºC and pH 9−10). From Savage *et al.* (2010).

Mineral	Estimated rate constant, log k (mol m^{-2} s^{-1})	Modified rate constant, log k (mol m^{-2} s^{-1})
Analcime	−17.0	−17.0
Celadonite	−16.0	−17.0
Clinoptilolite	−17.0	−17.0
K-feldspar	−17.3	−18.3
Mg-montmorillonite	−16.0	−16.0
Na-montmorillonite	−11.0	−11.0
Phillipsite	−14.0	−20.0

TABLE 2. Summary of reaction products documented from cement–aggregate reactions in old concretes.

Structure	Age (y)	Aggregate	Reaction products	Source
Gun battery	110	Granite	Crystallized alkali-silica gel (okenite) in cracks in aggregate	(Peterson *et al.*, 2006)
Dam wall	65	Greywacke	Alkali-silica gel in reaction rims on aggregate grains, occasionally crystallized into rosette/bladed crystals	(Blackwell and Pettifer, 1992)
Dam wall	60	Dacite	Alkali-silica gel and/or K-, Na-substituted C-S-H mineral (okenite?) in reaction rims on aggregate grains	(Shayan, 1988)
Dam wall	50	Granite	Alkali-silica gel, turning to zeolite-like needles on exposure to air	(Fernandes *et al.*, 2004)
Power station	40	Siliceous limestone	Alkali-silica gel lining voids and cracks	(Grattan-Bellew, 1995)
Dam wall	30	Siltstone, sandstone	Alkali-silica gel lining pores, with K-, Na-substituted okenite in reaction rims on aggregate grains	(Cole *et al.*, 1981); (Cole and Lancucki, 1983)
Dam walls, bridge	15–50	Granites; alluvial sediment	Alkali-silica gel in reaction rims on aggregate grains	(Fernandes, 2009)
Road pavement	3–18	Quartzite, granite, schists	1 mm reaction rims of the zeolite erionite (KNa-$CaAl_4Si_{14}O_{36}.8H_2O$) on aggregate grains; ettringite in voids	(Marfil and Maiza, 2001)
Dam wall, bridges, road pavement, quays, median road barriers	5–70	Siliceous limestone, rhyolitic tuff, quartzite	Alkali-silica gel in reaction rims on aggregate grains, occasionally with rosettes of unidentified crystalline material	(Bérubé and Fournier, 1986)
Bridges	?	Not specified	Calcium-alkali-silica gel in reaction rims on aggregate grains	(Brouxel, 1993)
Buildings	?	Greywacke	Smectite-type clay in cracks in aggregate grains	(Hünger *et al.*, 1994)
Bridge, railway sleepers, pile, airport runway	1–3	Dolomite	De-dolomitization reactions with calcite and brucite as products	(Deng *et al.*, 1993)

calcite and gypsum precipitates. Within the perturbed zone, there is an overall decrease in Si and Al and an increase in Ca and Mg. A zone of calcite, which is 2 mm thick, occurs within the concrete at the contact with mudstone (Tinseau *et al*., 2006).

Evidence from alkaline oil floods is shown in Table 3. Results from a deltaic sandstone reservoir in the White Castle Field, Louisiana, USA, using a mixed slug of sodium carbonate-sodium silicate solution suggest that scaling of production wells was caused by calcite, rather than silicate mineral precipitation (Falls *et al*., 1994). Nineteen percent of the total alkali injected (equal to 5.1% of the slug volume) was consumed by reaction in the reservoir. Wells were 60 m apart. Calcite and silica scales were observed in production wells after a 3-year alkaline flood in a sandstone reservoir in the Daqing oilfield in China (Yang *et al*., 2003). Further studies of a 2-year alkaline flood (with surfactant) in Block N-1DX of the Daqing Field, China (Wang *et al*., 2004) showed severe scaling of production wells and pumps. Wells were 250 m apart, contacting 0.75 km^2 of the reservoir. Mineralogical analysis of the scale showed that its characteristics were time-dependent, with carbonates dominating initially, and then silica scale. In a third phase, the Si concentration of produced fluids increased from 289 in March 2000 to 430 mg/l in May (the initial content was 0.6 mg/l). Krumrine *et al*. (1985) also noted time-dependent scale compositions in an alkaline flood of the Long Beach Unit of the Wilmington Field, California, caused by mixing of saline waters from one zone with alkaline water from other zones. Alkaline flooding was carried out between March 1980 and December 1983, using sodium silicate, sodium hydroxide and salt solutions. Krumrine *et al*. (1985) believe that the type of scale was controlled by the pH of the system. Hydroxide precipitates were observed to age from amorphous to more crystalline forms during the course of a flood. Until late-1982, the pH of produced fluids was <8, but a steep increase to pH >9 at the end of 1982 caused the silica content of produced fluids to increase from <4000 mg/l to >8000 mg/l. This was accompanied by a change from calcite to magnesium silicate scaling of production equipment. Scales identified in 1983 consisted mainly of amorphous silica (Krumrine *et al*., 1985).

At Maqarin, despite the variation in the primary lithologies and mineralogy of the host rocks, the alkaline alteration mineralogy in both the Eastern Springs and Western Springs areas is very similar (Baker *et al*., 2002). The principal alteration products at both sites include: ettringite and thaumasite (and ettringite-thaumasite solid solutions); poorly-crystalline or amorphous C-S-H gels; and poorly-crystalline or amorphous 'zeolitic composition' or calcium aluminosilicate hydrate (C-A-S-H) gels, although the latter form a small proportion of the overall parageneses. Mineral parageneses have been interpreted by Baker *et al*. (2002) as providing confirmation of the scheme of mineral alteration originally described by Savage (1998).

A marked feature of the diagenesis of mudstones and volcanic tuffs around saline, alkaline lakes is the strong zonation of minerals (Surdam and Sheppard, 1977; Hay, 1977; 1986). There is a concentric pattern of alteration of tuffs from (moving inwards) unaltered glass, through alkalic, silicic zeolites (e.g. clinoptilolite) to analcime, and finally to K-feldspar. The tuffs or mudstones are altered to zeolites, K-feldspar, clay minerals (smectite, celadonite, illite, palygorskite) and silica. The zeolites are mainly analcime,

TABLE 3. Summary of reactions observed in alkaline flooding tests in hydrocarbon reservoirs.

Field	Time (y)	Distance, m (Area, m^2)	Reaction products	Source
Daqing, China	3	250 (8×10^5)	Calcite and silica.	(Yang *et al*., 2003)
Daqing, China	2	250 (8×10^5)	Carbonates initially, then silica scales.	(Wang *et al*., 2004)
White Castle, Lousiana, USA		60 (6×10^3)	Calcite.	(Falls *et al*., 1994)
Wilmington, California, USA	3	(8×10^5)	Calcite, Mg-silicates and silica.	(Krumrine *et al*., 1985)

clinoptilolite, erionite, phillipsite, mordenite and chabazite. At Searles Lake, smectite shows no alteration to secondary minerals at pH $\leqslant 9$, but in the pH regime 9–10, it is progressively replaced by a mixture of Fe-illite, Mg-montmorillonite, analcime, clinoptilolite (rare) and K-feldspar (Hay and Moiola, 1963; Hay *et al.*, 1991). Unfortunately, there are no mineral textural data to indicate whether any of these minerals replace each other (i.e. whether an Ostwald step sequence is defined). Savage *et al.* (2010) had reasonable success in reproducing secondary mineral distributions, apart from an absence of analcime in the results of their simulations.

Fracture-filling minerals in some granitic rocks show similar mineral sequences to those hypothesized to occur due to hyperalkaline alteration, but as a result of variations in temperature, rather than pH. For example, laumontite, a Ca-zeolite which is thought to occur at distal edges of the hyperalkaline plume, can occur with clay, quartz and calcite as a low-temperature (<100ºC) filling in fractures in granite (Savage *et al.*, 1987). Sandström *et al.* (2009) report quartz, chlorite-corrensite, calcite and pyrite overprinting vein coatings of laumontite in fractures in Forsmark granite in Sweden. These authors also report the growth of K-feldspar, albite and analcime (also typical minerals of hyperalkaline alteration) accompanying quartz in this particular phase of alteration at Forsmark (‘Generation 3’ of Sandström *et al.*, 2009), which they estimate to have occurred at a temperature of 100ºC or so. Consideration of a thermodynamic stability diagram for sodium and calcium aluminosilicates (Fig. 3) shows that at pH 8, increasing temperature from 15 to 100ºC, will move stability fields from kaolinite, through analcime, to laumontite. This is the same sequence of alteration minerals hypothesized for migration of the alkaline plume at low temperature. Laumontite is stabilized relative to analcime by higher temperature or a low Na^+/Ca^{2+} ratio in a coexisting fluid or both. From a theoretical perspective, analcime and laumontite are stabilized by pH >8, with their relative predominance controlled by the Na^+/Ca^{2+} ratio of the fluid. Higher temperature stabilizes laumontite relative

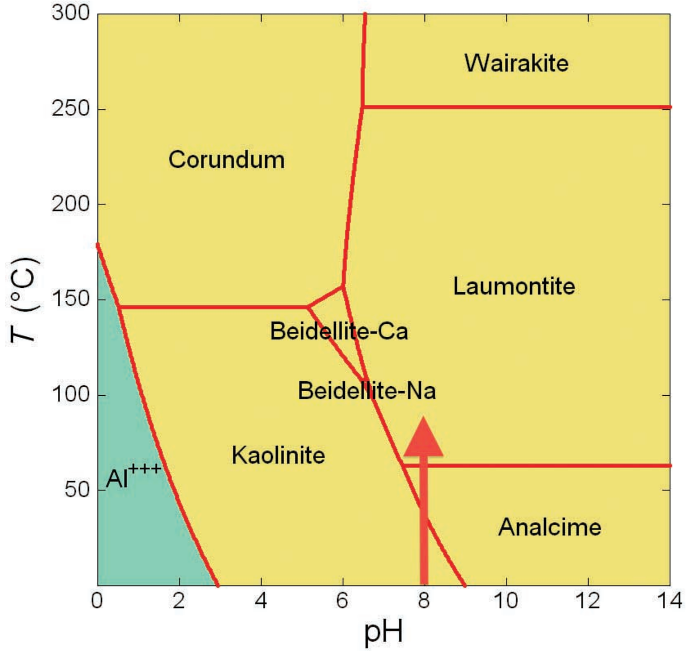

FIG. 3. Activity diagram of minerals in the system $Na_2O–CaO–Al_2O_3–SiO_2–H_2O$ at variable temperature and pH using *Geochemist's Workbench* (Bethke, 2008). The arrow denotes a hypothetical heating curve, showing that kaolinite can be transformed to analcime and then to laumontite through heating alone at pH = 8 and is analogous to reactions occurring at high pH at ambient temperature. $SiO_{2(aq)}$ and Al^{3+} activities are defined by quartz and kaolinite, respectively. $Ca^{2+} = 10^{-2}$ mol/l. $a(Na^+)^2/Ca^{2+} = 2$. Database = thermo.com.V8.R6.230.

to analcime. These thermodynamic consideration confirm that the mineral sequences observed in fracture fillings at Forsmark described by Sandström *et al*. (2009) reflect decreasing temperatures and produce a sequence which is the reverse of that hypothesized for an advancing front of hyperalkaline alteration (Fig. 1).

Porosity-permeability modification

The porosity of groundwater flow paths and components of the EBS (buffer, tunnel backfill) may change as a consequence of alkaline alteration due to primary minerals dissolving and the accompanying precipitation of secondary minerals (Lichtner and Eikenberg, 1994). Moreover, the sealing of porosity through alkaline alteration may hinder the release of gas from the repository, or lead to 'pulsing' of gas release as fractures close and re-open due to pressure build ups (Metcalfe and Walker, 2004). Re-opening of porosity could lead to further migration of hyperalkaline fluids. Changes in permeability are likely to accompany any change in porosity, but there is no simple relationship describing their interdependence. The Kozeny-Carman relationship has been used to link these changes (e.g. Soler *et al*., 2006):

$$K = \mathrm{c}\frac{\varepsilon_f^3}{(1-\varepsilon_f)^2} \tag{9}$$

where K = hydraulic conductivity, ε_f is the flow porosity and the constant c has to be deduced from initial conditions for porosity and hydraulic conductivity and depends on the solid composition and structure. However, the application of this relationship depends upon specific calibration to the system under study and thus cannot be applied *a priori* (e.g. Kosakowski *et al*., 2009).

Moreover, it is important for predictive modelling (especially in fractured rocks) to have a better understanding of how porosity/fractures may be occluded due to the precipitation of neoformed minerals. Currently, models assume that porosity is filled in a given cell volume with disregard to how precipitation may occur. For example, it is likely that new aluminosilicate minerals would precipitate on (cannibalize) existing aluminosilicates, due to the relative insolubility of aluminium. However, the greater solubility of aluminium at pH greater than neutral may encourage precipitation uncontrolled by pre-existing minerals. Studies of fracture fillings in granite (and similar rock types) could thus be rewarding in this regard.

Analogue evidence

Confidence regarding positive solid volume changes during alkaline alteration may be gained from cement–aggregate reactions in that solid volume expansion is noted in all studies of this type, across a range of aggregate types, which is manifested in concrete structures by cracking, buckling, pop-outs and extrusion of joint-filler (Gillot, 1995). However, quantitative measurements of the change in physical properties of concrete due to cement-aggregate reaction have not been acquired.

There is considerable evidence from the oil industry regarding porosity-permeability changes during alkaline flooding. Common features are erosion and degradation of gravel packs around injection well-bores, enlargement of injection well-bores and scaling and permeability reduction in production well-bores (Okoye *et al*., 1991). To a degree, this is accentuated by higher than ambient temperatures in the reservoir formations concerned. However, in a field test of alkali flooding during oil-reservoir remediation, Cook *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. It should be noted that alkaline slugs introduced during floods contain no calcium and are NaOH-KOH-based fluids, and are thus designed not to decrease porosity in the formation injected.

Measurements of physical properties at Tournemire show an increase in porosity in the 15-year old cement and concrete in the first 2 cm from the contact with mudstone (from 60 to 68%) due to dissolution of portlandite and a decrease in porosity of the first cm of mudstone (from 8 to 5%) (Tinseau *et al*., 2008). The modelling study of De Windt *et al*. (2008) confirms that mineralogical transformations would lead to significant porosity loss (approaching zero porosity) only a few millimetres from the cement–mudstone interface after a few years of interaction.

Studies at Maqarin have demonstrated significant reduction in the matrix porosity of the basalt and chert-rich fluvial gravel and colluvium through cementation with gels and zeolites (Baker *et al*., 2002). These observations suggest that reactions occurring in a repository in aluminosilicate-rich rocks will therefore tend to produce sealing and reduction in porosity (Baker *et al*., 2002). Observations at Maqarin also show that interaction with alkaline groundwater can produce narrow (1–5 mm wide) zones, adjacent to fracture walls, in which the microporosity is enhanced by the dissolution of calcite and dolomite. These alteration zones are complex, and the inner margin (furthest from the fracture wall) of the leached zone is typically marked by a narrow front (1–2 mm wide) along which porosity is again reduced by secondary calcite cementation (Baker *et al*., 2002). Moreover, there is evidence for both repeated fracture sealing operating on timescales of tens to hundreds of years and for the long-term stability of newly-formed minerals measured in thousands of years. Fracture sealing may occur extensively and over short timescales with calcic fluids (tens to hundreds of years) at Maqarin (Smellie, 1998). The episodic reactivation of fractures, accompanied by the rejuvenation of hyperalkaline groundwater flow, complicates the sequence of mineral precipitation and alteration observed in the veins.

Conclusions

Analogue systems (and operative timescales) relevant to the understanding of the alkaline disturbed zone include: industrial analogues, such as alkaline flooding of hydrocarbon reservoirs (up to 30 y), cement-aggregate reactions (up to 100 y) and the Tournemire tunnel (up to 125 y); and natural analogues, including the hyperalkaline springs at Maqarin, Jordan (>100,000 y), saline, alkaline lakes (>1,000,000 y) and fracture fillings in granite (>1,000,000 y). These systems show that alkaline alteration can be observed for thousands of years over distance scales of hundreds of metres under extreme conditions of hydraulic gradients in fractured rocks (Maqarin), but may be limited to a few centimetres over tens to a hundred years in mudstone (Tournemire).

Important reaction mechanisms for retardation of alkaline fluids include: fluid mixing (alkaline oil floods, Maqarin); ion exchange (alkaline oil floods, Tournemire); and kinetic mineral hydrolysis reactions (all systems studied). Qualitative and quantitative kinetic data for mineral reactions are available from cement aggregate reactions and the Searles Lake analogue.

These systems show that alteration minerals are likely to consist of a sequence of calcium (aluminium) silicate hydrates, zeolites, silica polymorphs, sheet silicates (e.g. illite, palygorskite), feldspar and carbonates. Short-term alteration observed in cement-aggregates is characterized by C-S-H minerals and incipient zeolite formation, whereas evidence from the Tournemire tunnel shows the growth of K-feldspar after relatively short time intervals (tens to a hundred years), which may be due to its occurrence as overgrowths on pre-existing K-feldspar crystals (i.e. without the requirement for the slow step of nucleation). Observations from natural analogue systems (Maqarin, saline, alkaline lakes, fracture fillings in granite) demonstrate that zeolitic alteration, although generally absent from short-term laboratory experiments, can take place over timescales relevant to radioactive waste safety assessment.

Alkaline alteration tends to result in porosity decreases, except where reactant fluids are calcium-free (e.g. near-injection well interactions in alkaline oil floods) and some incipient alteration in the rock matrix adjacent to fractures (e.g. at Maqarin). Fracture sealing may occur extensively and over short timescales with calcic fluids (tens to hundreds of years). Data concerning mechanisms of porosity closure may be obtained from a more extensive study of fracture fillings in granite and similar rocks.

Data from industrial and natural analogues may thus supply some key data for bridging time and space scales between laboratory and *in situ* experiments on one hand and the requirements for safety assessment on the other.

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