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Chen, X, Thornton, SF and Small, J (2015) Influence of Hyper-Alkaline pH Leachate on Mineral and Porosity Evolution in the Chemically Disturbed Zone Developed in the Near-Field Host Rock for a Nuclear Waste Repository. *Transport in Porous Media*, 107 (2). pp. 489-505. ISSN 0169-3913

<https://doi.org/10.1007/s11242-014-0450-0>

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Influence of hyper-alkaline pH leachate on mineral and porosity evolution in the chemically disturbed zone developed in the near-field host rock for a nuclear waste repository

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Abstract:

This paper evaluates the effect of hyper-alkaline (NaOH/KOH) leachate on the mineralogy and porosity of a generic quartzo-feldspathic host rock for intermediate- and low-level nuclear waste disposal following permeation of the cementitious repository barrier by groundwater. The analysis is made with reference to expected fluid compositions that may develop by contact of groundwater with the cementitious barrier to form a chemically disturbed zone (CDZ) in the adjacent host rock, as informed by relevant natural analogue sites. Theoretical analysis and numerical modelling is used to explore the influence of different host rock mineral assemblages on changes in pore fluid chemistry, multiple mineral dissolution and precipitation reactions and matrix porosity within the CDZ under these conditions. The numerical modelling accounts for kinetic and surface area effects on the mineral transformation and porosity development for periods of up to 10000 years travel time from the repository and ambient temperature of 20° C. The analysis shows that dissolution of quartz, feldspar and muscovite in the host rock, by the hyper-alkaline waste leachate, will create relatively high concentrations of dissolved Si and Al in the pore fluid, which migrate as chemical fronts within the CDZ. Precipitation of secondary mineral phases is predicted to occur under these conditions. The increase in matrix porosity that arises from dissolution of primary aluminosilicate minerals is compensated by a reduction in porosity due to precipitation of the secondary phases, but with a net overall increase in matrix porosity. These coupled physical and geochemical processes are most important for contaminant transport in the near-field zone of the CDZ and are eventually buffered by the host rock within 70 m of the repository for the 10000 year travel time scenario. The predicted changes in matrix porosity may contribute to increased transport of radionuclides in the host rock, in the absence of attenuation by other mechanisms in the CDZ.

Keywords: nuclear waste disposal, mineral evolution, porosity changes, sandstone, CDZ

1 Introduction

The expected disposal of UK intermediate level nuclear waste in a subsurface engineered repository requires consideration of the fate and transport of contaminants in the geosphere following eventual failure of waste containers and barrier components and release of mixed waste leachate from the repository. Failure of the barrier components will result in a hyper alkaline plume, formed by permeation of groundwater through the cementitious barrier and wastefrom into the near-field environment around the repository. The migration of the hyper-alkaline plume creates a chemically disturbed zone (CDZ), which is an important interface for geochemical, mineralogical, biological and physical transformations and reactions between components in the waste leachate and the host rock around the repository. The CDZ is characterised by steep biogeochemical gradients within the near field of a nuclear waste containe, and may provide a critical control on behaviour and transport of radionuclides in the waste leachate.

The alkaline leachate composition will evolve over time as different mineral phases in the cementitious barrier contribute to reactions with groundwater. It is necessary to understand how this dynamic chemical system affects the mineralogical and porosity evolution of the host rock to evaluate the impact on contaminant migration and attenuation within the CDZ, to support a safety case for repository design and understand the environmental risk of barrier failure. This behaviour includes dissolution and precipitation of mineral phases as the alkaline pH leachate composition evolves over time. It will likely involve several cycles of precipitation and re-dissolution of mineral phases, whose geochemical stability is controlled by the leachate chemistry and leachate-mineral reactions. In turn, this will influence the porosity evolution of the host rock as mineral phases are developed over time, with related affects on fluid permeability and element cycling.

Laboratory batch and column experiments are typically used to investigate geochemical processes and mineralogical transformations that occur in geological materials impacted by high alkaline pore fluids (Corkhill et al., 2013). While these provide the essential conceptual understanding and parameter values for numerical modelling studies, there is a need to up-scale these observations to interpret the effect of variation in hyper-alkaline leachate composition on porosity and mineralogical evolution in the CDZ over representative time-scales in the near field host rock around a deep geological nuclear waste repository. This can be conveniently achieved by considering scenarios developed from related laboratory studies as a natural analogue of the CDZ evolution in a

representative waste repository host-rock composition. Generally, a natural analogue is defined as 'an occurrence of materials and processes which resemble those encountered in a proposed geological repository' (Chapman, 1986; Milodowski, 2009). Currently, research on natural analogues of alkaline plumes has focused on two examples, at Khushaym Matruk and Maqarin in Jordan. At the Khushaym Matruk site the influence of high-alkaline solutions on a natural argillaceous formation has been studied as a natural analogue of a clayey barrier (Techer et al., 2006), while studies at the Maqarin Natural Analogue Project site have focused on the characterisation and evolution of hyper-alkaline leachate pore fluids over time (Khoury et al., 1992; Alexander et al., 1992; Clark et al., 1994).

This site provides a rare opportunity to examine the influence of cement pore fluids on radioactive and chemotoxic wastes, when influenced by the dissolution of calcium silicate hydrate gel phases and portlandite. Several investigations have been conducted at the Maqarin site as a consequence of increased interest in deep geological disposal of nuclear waste (Alexander et al. 1990; Linklater 1998; Smellie, 1998). These have deduced three different hyperalkaline groundwater compositions, denoted as "Western Springs" (early, active, high-pH NaOH/KOH leachate), "Eastern Springs" (intermediate, active, lower pH $\text{Ca}(\text{OH})_2$ -buffered leachate) and "Daba Region" (late, inactive (fossil), lower pH silica-dominated leachate), which are believed to be analogous to three different stages in the theoretical evolution of a cementitious repository for the disposal of low- to intermediate-level nuclear wastes. This chemical evolution is shown schematically in Figure 1.

Several studies have examined the interaction of high-pH plumes with geological materials (e.g. rocks and clays used in engineered barriers for radioactive waste containers) from different perspectives (Adler et al., 1998; Steefel and Lichtner, 1998; Soler, 2003). These include the effects of high-pH fluids on fractured rock (Berner, 1998; Neall, 1994a; Neall, 1994b) and modelling interactions between hyperalkaline fluids and bentonite (Savage et al., 2002). The latter study found that porosity changes may occur in the host matrix due to precipitation of secondary phases under such conditions.

However, few studies have combined the coupled influence of porosity change and high-pH leachate with multiple kinetic chemical reactions and mineralogical dissolution in geological materials that may represent the generic composition of a host rock for a deep GDF. The aim of this study is to examine the effect of high pH leachate (similar to the "Western Springs" composition mentioned above) on mineralogical transformations and porosity evolution that may occur in the geosphere as the hyper alkaline plume develops within the CDZ adjacent to a GDF, following failure of the containment barrier. Sandstone was used for experimental reasons in laboratory studies supporting

this modelling work to represent a generic rock composition. The sandstone is mineralogically and geochemically similar in basic composition to low permeability geological materials which are expected to be a host rock for a GDF. Attention in the modelling study is focused on the quantitative description of geochemical reactions, mineralogical transformations and matrix porosity changes that occur as a high-pH Na/KOH leachate breaks through sandstone in column experiments. Other chemicals in the initial leachate such as Ca^{2+} have been assumed absent in this study, due to very low content in the leachates used.

2 Leachate and host rock composition

The high-pH (NaOH/KOH) leachate which originates from the cementitious barrier in the repository after groundwater breakthrough has the Western Spring composition in the Maqarin site as a natural analogue (Fig 1). In the present study the fluid representing this chemical composition (NaOH = 5.2g/l and KOH = 3.8g/l) was designated Young Cement Leachate (YCL) and used with the sandstone sample (below) in column experiments completed by the British Geological Survey within the BIGRAD consortium. The background water saturating the sandstone column before YCL breakthrough is assumed to be pure water for simplification. Permo-Triassic sandstone from the Bromsgrove Formation in the UK Midlands was used to represent a generic host rock mineralogy and geochemistry for the modelling study, with a bulk composition shown in Table 1.

3. Modelling approach

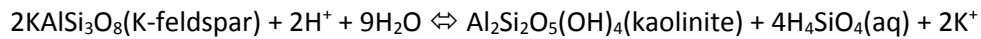
3.1 Mineral assemblage considered

The geochemical code PHREEQC (Parkhurst and Appelo, 2010) and coupled analysis software Toughreact (Xu et al., 2006) were used to perform the numerical simulations in this study. The main primary minerals in the sandstone matrix are quartz (75.5%) and K-feldspar (16%). As quartz is the dominant primary mineral and could play an important role in the phase dissolution, numerical simulations were first performed for transport of YCL through a column comprising quartz only. Simulations of YCL transport through a quartz column with K-feldspar added were then completed to observe the influence of this phase on the mineral equilibria. Other minor minerals, such as Illite/chlorite/smectite (3.7%), kaolinite (3.5%) and muscovite (0.7%) were included in later simulations. However, based on the results of the linked laboratory studies phlogopite (0.2%), apatite (0.2%) and TiO_2 (0.3%) were excluded due to their very low percentage in the sandstone and limited influence on the geochemical process observed.

Potential secondary minerals that may develop within the hyper-alkaline plume were selected according to field and experimental observations, and also from equilibrium geochemical model

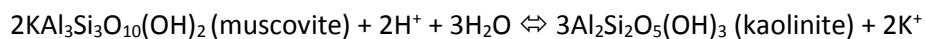
calculations made using PHREEQC. These phases were allowed to precipitate if conditions allow. For the primary minerals, the relationship between K-feldspar, kaolinite and muscovite may be considered a series of weathering reactions described by acid-base reactions (Weaver, 1989; Appelo and Postma, 2010), presented below.

(1) K-feldspar (primary mineral) forming kaolinite (secondary mineral)

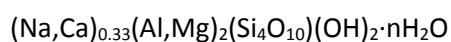


Kaolinite is normally formed by weathering or hydrothermal alteration of aluminosilicate minerals. Rocks rich in feldspar commonly weather to kaolinite.

(2) Muscovite (primary mineral) may also react to form kaolinite, based on experimental evidence (Kiryukhin et al., 2008)



As a high temperature secondary phase, kaolinite may form under temperatures of 70°C (Kiryukhin et al., 2008), but this reaction is unlikely for a Intermediate-Level Waste or Low-Level Waste (I/LLW) disposal scenario with a temperature around 25°C. Kaolinite was therefore not included as a secondary phase. Other clay minerals in the sandstone include the illite group and smectite group (3.7%), in which smectite is the only swelling mineral. The most common smectite mineral is montmorillonite, with the general chemical formula :



Montmorillonite potentially increases greatly in volume when absorbing water to change the host matrix porosity. As it often occurs intermixed with muscovite, illite, and kaolinite, it has great potential to be a secondary phase in sandstone. Smectite group clays, including pyrophyllite, montmorillonite, beidellite, nontronite, talc, saponite, hectorite and saunonite etc were also studied.

3.2 Reactive transport and kinetics of mineral evolution

3.2.1 Reactive transport

Flow according to Darcy's Law was used in the transport modelling. The modified version of Darcy's Law, which includes chemical osmosis and thermo osmosis (Chen et al., 2013; Chen and Hicks, 2013), was not included here to simplify the discussion. Fractures were not considered in the analysis as the

experimental columns were re-packed disaggregated sandstone with intergranular flow. The general formulation which describes chemical transport in porous media is (Appelo and Postma, 2010):

$$\frac{\partial (f C_i)}{\partial t} = \frac{\partial}{\partial x_a} \left(\frac{\partial C_i}{\partial x_b} D_{ab} \right) - \frac{\partial (u_a C_i)}{\partial x_a} + Q \quad (1)$$

in which C_i is the i th chemical component, u_α is the Darcy velocity in α direction ($\alpha=1, 2$ or 3 which is the space coordinate), f is the porosity and Q is the sorption or reaction term.

3.2.2 Kinetics and rates of multiple mineral dissolution or precipitation

As mineral dissolution and precipitation kinetics may exert a strong control on the mineralogical and geochemical evolution of the CDZ, this section introduces how the rates, surface area, temperature dependence, precipitation and porosity changes must be considered in the analysis. The dissolution rate of minerals is controlled by the temperature and pH. This is normally obtained from experiments (Appelo and Postma, 2010). The overall rates can be described as (Appelo and Postma, 2010):

$$R_k = r_k \frac{A_0}{V} \left(\frac{m_k}{m_{0k}} \right)^n \quad (2)$$

in which r_k is specific reaction rate, $\frac{A_0}{V}$ is the initial surface area (m^2) /amount of solution (kgw) ; $\left(\frac{m_k}{m_{0k}} \right)^n$, moles of solid at a given time/initial moles of solid (this is to account for changes in A_0/V) ; for uniformly dissolving spheres and cubes $n=2/3$ (normally for experiment) .

Specific surface area

Surface area is an important parameter which influences the kinetics of dissolution and precipitation, heterogeneous catalysis, adsorption and surface reactions. It denotes the total surface area of a mineral per unit of mass (m^2/kg), solid or bulk volume (m^2/m^3 or m^{-1}). The surface area of a single mineral can be obtained experimentally, but remains a challenge for a multiple mineral assemblage such as the sandstone used in this study. In this case the surface area used for minerals was based on the literature, taken either from experimental studies or from published modelling assumptions. Sonnenthal and Spycher (2001) used a cubic array of truncated spheres making up the framework of rock to estimate mineral reactive surface areas. (Nagy, 1995) increased surface areas of clay minerals such as kaolinite, illite and smectite based on the smaller grain sizes of these sheet silicate

minerals. The surface areas used in the present study (Table 2) were taken from Nagy (1995) and reduced by one order of magnitude in the numerical simulations to account for the difference between the reactive surface areas calculated from grain size and those of the hydrologically accessible mineral surface area (Xu, 2004; Tianfu et al., 2006; Xu et al., 2010).

Temperature dependence

As rate r_k may be constant at a fixed temperature, then it is normally called a rate constant. However, it is a highly temperature dependent coefficient, but as most rate constants are reported at 25°C, it may be convenient to approximate the dependency of the rate constant as a function of temperature (Steefel and Lichtner, 1998).

Mineral precipitation

Mineral precipitation processes are very complex and include nucleation, crystal growth, Ostwald ripening processes and the calculation of the reactive surface area, which are quite different from dissolution processes (Steefel and van Cappellen, 1990). Such processes for mineral precipitation are not considered in this paper. No precipitation rate data exist from experiments for most minerals and in this study the precipitation kinetics were assumed to be the same as that of dissolution.

Porosity changes

Mineral precipitation and dissolution may strongly affect porosity in the host porous media (Xu, 2004; 2008; Tianfu et al., 2006). The molar volumes of secondary phases generated by hydrolysis reactions are often larger than those of the primary reactant minerals. For example, zeolites or clays, which may be secondary hydrous phases of feldspars reacting with aqueous fluids, have a larger molar volume than feldspars. Such process may then reduce the matrix porosity.

4. Conceptual model

The conceptual model developed for the scenario considered in this study consists of a 100m 1-D numerical model domain with a homogeneous sandstone matrix and steady-state transport of YCL for different time periods (Figure 2). 100 cells have been used for the 100m model (1m/cell), with a time step of 1.E08 s. The flow rate was set at 1E-3 m/yr, giving a simulated timescale around 10000 years. The YCL was injected from the left side with flow out from the right side. Tables 1-3 show the parameters required for the modelling. The following components were included in the numerical simulations :

- (1) Mixing of a high-pH plume with background groundwater
- (2) High-pH alkaline plume transport with consideration of multiple chemical reactions
- (3) Kinetic dissolution and precipitation of multiple primary minerals

(4) Kinetics precipitation of multiple secondary minerals

(5) Mineral dissolution and precipitation coupled with mineral volume changes

(6) Volume change coupled with flow and transport

5 Results and discussion

To give a full understanding of YCL interactions with minerals in the sandstone, the following analysis has been divided into four sections with added complexity in each subsequent section. As quartz is present at 75% in the sandstone Analysis 1 assumes that the sandstone contains quartz only; in Analysis 2 the second most important mineral in the sandstone, K-feldspar, has been included; in Analysis 3 other minerals such as kaolinite, muscovite and illite have been included in the numerical simulations. The results are presented for simulated timescales of 10, 100, 1000 and 10000 years.

Analysis 1: YCL transport through porous media containing quartz

YCL transport through quartz sand was first studied to assess the influence of only this mineral on phase transformations. A numerical batch experiment with sufficient quartz dissolving into YCL was studied first using PHREEQC to find the potential secondary phases. As YCL only contains K, Na and OH, with very little Ca, no secondary mineral phase precipitated.

In this simulation YCL transport results in a progressive increase in pore fluid pH and Na^+ along the flow path over time from 10 to 10000 years (Figure 3a and b). Quartz dissolves into the YCL following a kinetic reaction, which increases the Si concentration. This forms a "Si wave" which migrates to the far-field of the host rock over time (Figure 3c). Due to the quartz dissolution, the matrix porosity increases over time (Figure 3d). The porosity increases in the near-field of the GDF much more than in the far-field. This feature moves progressively into the far-field over time. The corresponding quartz volume shrinkage is shown in Figure 3e. The influence of quartz dissolution on the pore volume change increases over time and is much stronger in the near-field (0-3m) than the far-field (>3m).

Analysis 2.1 : YCL transport through porous media containing quartz and K-feldspar

In this analysis, K-feldspar has been included in the modeling, with kinetic dissolution of both quartz and K-feldspar. YCL transport results in a progressive increase in pore fluid pH and Na over time from 10 to 10000 years (Figure 4a and b). The concentration of AlO_2 (not present in Analysis 1) increases over time from dissolution of the K-feldspar, forming a " AlO_2 wave", which propagates through the CDZ (Figure 4c). Figure 4d shows greater detail of the AlO_2 concentration changes in the near-field. It shows that AlO_2 will reach an equilibrium concentration of 0.0025 mol/L and then decrease, which may reflect precipitation of secondary phases. Figure 4e shows the K^+ distribution, which originates

from both the initial YCL concentration and also K-feldspar dissolution (the effect of the latter on the K^+ concentration cannot be resolved due to the high background value in the YCL). Quartz dissolution produces increased SiO_2 (aq), which forms a “Si wave” that migrates through the CDZ (Figure 4f). Significant quartz dissolution and increase in concentration of Si will occur in the near-field of the GDF (Figure 4g). The overall porosity change due to the combination of dissolution and precipitation will still increase, due to significant dissolution of quartz and K-feldspar (Figure 4h). In the near-field (around 0-4m), the porosity changes significantly (Figure 4i). The volume change of K-feldspar in the CDZ occurs over the whole distance, but is more significant within the near-field close to the barrier (Figure 4j and 4 k).

Analysis 2.2 : Influence of K-feldspar on pH, Si and AlO_2

Analysis 1 and 2.1 compared the influence of YCL on quartz and quartz/K-feldspar in combination. The influence of K-feldspar on the reactions in the sandstone may be summarized in this section. Figure 5a compares the SiO_2 (aq) distribution in the quartz-only simulation in Analysis 1 with the influence of K-feldspar in Analysis 2.1. The labels “1000 yrs (with)”, in which “(with)” means with K-feldspar, the other without “(with)” is only for quartz. It shows that more Si is released in the near-field in the combined quartz and K-feldspar scenario. However, the Si peak is lower in the far-field than that in the quartz-only scenario, due to the predicted precipitation of Si-bearing secondary phases such as nontronite. The influence of K-feldspar on pH is evident in Figure 5b. The K-feldspar dissolution increases the pH and buffers it at a higher level relative to the quartz-only system.

Analysis 3 : Influence of quartz, K-feldspar, illite, kaolinite and muscovite

In this analysis illite (3.7%, $(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2,(H_2O)]$), muscovite (0.7%, $KAl_2(AlSi_3O_{10})(F,OH)_2$) and kaolinite (3.5%, $Al_2Si_2O_5(OH)_4$) have been included in the simulation. Other minerals present in very low amounts (e.g. phlogopite (0.2%), apatite (0.2%) and TiO_2 (0.3%)) have been excluded.

In this scenario, the pore fluid pH increases over time, as in Analysis 2, with the influence of K-feldspar dissolution (Figure 6a). The pore fluid SiO_2 (aq) concentration also increases due to quartz dissolution, again forming a “wave” that propagates through the rock (Figure 6b), qualitatively similar to the behaviour in Analysis 2. The pore fluid AlO_2 concentration increases slowly over time due to dissolution of K-feldspar (mainly), illite, muscovite and kaolinite (Figure 6c). In this scenario, muscovite is a primary mineral, (different from Analysis 2), and significant dissolution of muscovite is predicted to occur in the near-field (Figure 6d). Note that Figure 6d shows the volume change of muscovite, which only arises from significant dissolution of this mineral phase.

Potential secondary phases that may form from dissolution of the primary minerals in the rock may be deduced from the saturation indices predicted by the numerical model (Figure 6e and 6f, note the plots for the near-field are used here for clarity of illustration). Figure 6e shows the saturation indices for five major primary phases. Illite is in equilibrium and kaolite is undersaturated in the near-field, but these two phases are high temperature phases and unlikely to precipitate at the temperature expected in the scenario, which is around 20°C (Kiryukhin et al., 2008). Other secondary phases such as albite, nontronite-Ca, nontronite-K, nontronite-Na, clinoptiol, montmor-K, montmor-Ca, montmor-Na have been considered. The saturation indices for these phases at 10 years is shown in Figure 6f.

The overall porosity still increases over time (Figure 6g) due to the dissolution of quartz (Figure 6h) and K-feldspar (Figure 6i). This occurs even though there is precipitation of potential secondary phases, which increase in volume and acts to reduce the porosity. The Ca related montmor-Ca, Na and K does not precipitate due to the very low concentration of Ca^{2+} in the initial YCL.

6. Comparison with observations from the literature

The above theoretical and numerical analysis provides a deeper understanding of the mineralogical and porosity evolution of the high-pH plume breaking through the sandstone within the CDZ over a large relevant spatial and temporal scales. The behaviour of the mineral phases predicted in the scenarios modelled can be considered further by comparison with the results of experimental and modelling studies in the literature.

This study shows that the pore fluid chemistry, mineralogical phase changes and porosity evolution in this generic host rock are very sensitive to changes in the high pH of the waste leachate and that the temporal variation in dissolution/precipitation products depends strongly on the primary mineral phase composition of the sandstone. The interaction of high-pH cement pore fluids with quartzo-feldspathic rock has been investigated in a number of studies (Braney et al., 1993; Savage and Rochelle, 1993; Adler et al., 1998; Steefel and Lichtner, 1998; Pfingsten et al., 2006; Soler, 2003), with the attention on a few main aspects such as scaling kinetic data for minerals, porosity changes with either Ca-bearing fluids and Na- or K-bearing fluids and the influence of matrix diffusion.

An experimental study of the effects of an alkaline plume on Clashach Sandstone (which has a similar mineralogy to the Briomgrove sandstone) was investigated by Braney et al. (1993). The Clashach Sandstone (Scotland, U.K.) has a simple mineralogy, dominated by quartz with minor K-feldspar, illitic clay and iron oxide component. SEM observations of sandstone samples after completion of the experiment identified quartz and K-feldspar dissolution, in agreement with the

theoretical and numerical predictions presented in this paper. The increasing concentration of Si and Al from the dissolution of quartz and K-feldspar, and propagation of these dissolved species in “wave like” form during this phase transformation, which was predicted to occur in the long term and at a large scale according to the theoretical and numerical analysis undertaken in the present study, can also be observed at very small scale in this published experiment.

The potential secondary phases included in this study were selected from the Toughreact database (Xu, 2004; Xu et al., 2006; Kiryukhin et al., 2008). The numerical modelling predicted the formation of nontronite-K, with a saturation index close zero. Nontronite-K has been found to precipitate at high temperature in high-level nuclear waste disposal experiments (Abrajano et al., 1990; Fontanaud and Meunier, 1983), but this is unlikely for the low temperature conditions considered in the scenarios evaluated in the present study (Bischoff, 1972). Furthermore, Ca²⁺-bearing secondary phases, such as CSH gel, may precipitate under experimental conditions similar to those modelled in this study (Braney et al., 1993), but these were not predicted to form in the sandstone because the concentration of Ca²⁺ in the YCL was very small.

An interesting finding from this theoretical analysis is the predicted increase in host rock porosity during permeation with the hyper alkaline leachate. Sydansk (1982) observed a similar feature during flushing of sandstone with a hyper alkaline NaOH solution. Silicate mineral dissolution was found to be significant under these conditions, with formation of water-soluble silicates, including Na orthosilicate and *in situ* formation of aluminosilicate phases. These mineral changes led to weight loss in the sandstone, increased matrix porosity and changes in permeability close to the solution inlet. Previous studies using closed system (no-transport) reaction-path models have also confirmed porosity increases for Na-K-Ca-OH fluids and decreases for Ca(OH)₂ fluids (Savage and Rochelle, 1993).

The literature examples above provide convincing support for the observations made from independent but converging theoretical and numerical modelling perspectives in this study. Previous experimental studies have evaluated mineralogical transformations in sandstone under hyper alkaline conditions at the small (micro to meso)-scale. The results reported here are the first to explore the geochemical, physical and phase dissolution/precipitation reactions responsible for the combined mineralogical and associated matrix porosity changes that occur in a quartzo-feldspathic host rock at the field-scale, under conditions mimicking the CDZ that develops as highly alkaline K-rich pore fluids migrate from a I/LLW GDF.

Conclusion

This paper has examined the effect of hyper alkaline leachate (NaOH/KOH) on the mineralogy and porosity of a generic quartzo-feldspathic host rock for intermediate- and low-level nuclear waste disposal under conditions which simulate the development of a chemically disturbed zone (CDZ) as this leachate composition migrates into the host rock, over a period of up to 10,000 years. By considering a range of modelling scenarios with increasing mineralogical complexity of the host rock, the analysis has enabled the porosity evolution linked to sequential primary mineral dissolution and secondary mineral precipitation to be deduced, based on coupling between these physical and geochemical processes. The scenario modelling shows that mineralogical transformations during permeation with the high-pH leachate are dominated by dissolution of quartz and feldspar, leading to relatively high concentrations of Si and Al (both absent in the leachate) in the pore fluid, which migrate as chemical fronts within the CDZ. Other primary aluminosilicate minerals (muscovite) in the host rock are also predicted to dissolve in the high-pH leachate along the plume flow path. This creates conditions suitable for the precipitation of secondary mineral phases. The modelling predicted these secondary phases to include illite, kaolinite and nontronite, but this is unlikely under the low temperature (20°C) conditions considered and expected to exist at the field scale. Mechanistically, the dissolution of the primary aluminosilicate minerals creates additional porosity in the host rock, contributed mostly by the dissolution of K-feldspar and quartz. Mineral dissolution (based on mineral volume changes) is most intense and porosity development most significant in the near-field zone of the CDZ. This process develops progressively outward through the CDZ along the flow path of the high-pH leachate plume, but is eventually buffered by the host rock within 70 m of the repository over a simulated 10000 year period. The precipitation of secondary mineral phases provides a mechanism to reduce the matrix porosity, but in this case does not fully compensate for the increase in matrix porosity resulting from dissolution of the primary aluminosilicates. This combined dissolution-precipitation process results in a net increase in matrix porosity of the host-rock within the CDZ, which may promote increased migration of radionuclides, where other mechanisms do not exist to attenuate these contaminants. However, as the chemistry of the hyper-alkaline plume around the waste container is likely to evolve with time towards more Ca²⁺-rich compositions, as components in the cement barrier dissolve into the groundwater, the porosity increase may be a transient feature. This transition in waste leachate composition is expected to promote the formation of different secondary minerals, presumed to include CSH gel phases, which will affect the matrix porosity to a different extent. Further research is underway to evaluate the significance of such Ca²⁺-rich plumes (which resemble the Easter Spring in the natural analogue in Jordan), on the mineralogical and porosity evolution in a generic host rock.

Acknowledgement

The authors acknowledge financial support from NERC in the project *Biogeochemical Gradients and RADionuclide transport* (BIGRAD; Grant Reference NE/H006464/1) for the completion of this work.

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Table 1 Composition of sandstone and conceptualization used in numerical model simulations

Mineralogy	Modal composition (%)	Modelling approach ¹
Quartz	75.5	Modeled (kinetics)
K-feldspar (KAlSi ₃ O ₈)	16.0	Modeled (kinetics)
Albite (NaAlSi ₃ O ₈)	0.0	Modeled (kinetics)
Illite/chlorite/Smectite	3.7	Modeled (Illite only, kinetics)
Kaolinite (Al ₂ Si ₂ O ₅ (OH) ₄)	3.5	Modeled (kinetics)
Dolomite	0.0	No
Calcite	0.0	No
Muscovite	0.7	Modeled (kinetics)
Biotite	0.0	No
Phlogopite	0.2	Not modeled
Zircon	0.0	No
Apatite	0.2	Not modeled
TiO ₂	0.3	Not modeled
Ilmenite	0.0	No
Magnetite	0.0	No
Fe oxide/oxyhydroxide	0.0	No
Porosity	18.4	18.4 (modeled)

Notes

1. Denotes whether mineral phase is included in model simulations and form of reaction rate used

Table 2. Physical parameters of minerals used in numerical model simulations

Mineral	Volume fraction ¹	Grain radius (m) ²	Surface area (cm ² /g mineral) ²
Quartz	75.5	0.001	9.8
K-feldspar	16.0	0.001	9.8
Illite	0.037	0.001	151.63
Muscovite	0.007	0.001	151.63
Kaolinite	0.035	0.001	151.63
Albite	0.0	NA	NA
Nontronite-k	0.0	NA	NA
Nontronite-na	0.0	NA	NA
Montmor-ca	0.0	0.001	5000
Montmor-k	0.0	0.001	5000
Montmor-na	0.0	0.001	5000

Notes

1. From British Geological Survey

2. From Sonnenthal et al. (2005) and Mukhopadhyay et al. (2009)

Table 3 Dissolution and precipitation of minerals)

Mineral	Activation energy (KJ/mol)	Rate constant K25 for dissolution(mol/m ² /s) ¹	Rate constant K25 for precipitation(mol/m ² /s)
Quartz	87.7	1.023E-14	1.023E-14
K-feldspar	38	3.89e-13	3.89e-13
Illite	35	1.66e-13	1.66e-13
Kaolinite	22.2	6.918E-14	6.918E-14
Muscovite	35.0	2.4E-13	2.4E-13

Notes

1. Precipitation and dissolution rates are assumed to be equal and are taken from Xu (2008), Xu et al. (2006), Xu (2004) Xu and Pruess (2001); Xu et al. (2000), Xu et al. (1999)

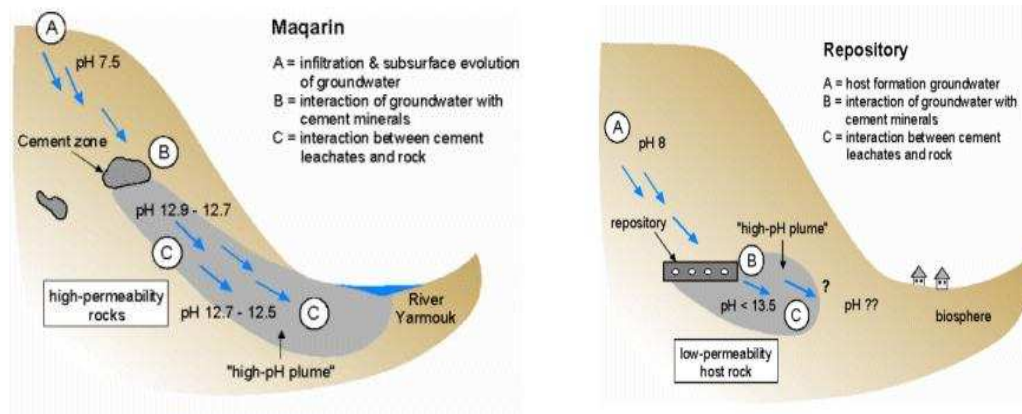


Figure 1. The Maqarin field site as a natural analogue of a hyper-alkaline plume developed in host rock from groundwater infiltration of the cementitious barrier of a repository at a GDF for intermediate-level nuclear waste (from Alexander and Mazurek, 1996)

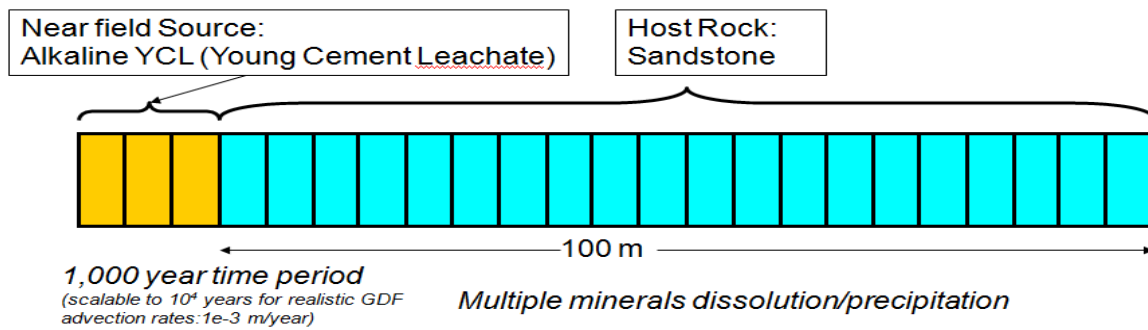


Figure 2. Conceptual model used in numerical modelling scenario of hyper-alkaline plume and CDZ developed in generic host rock for GDF (see text for discussion of input parameters)

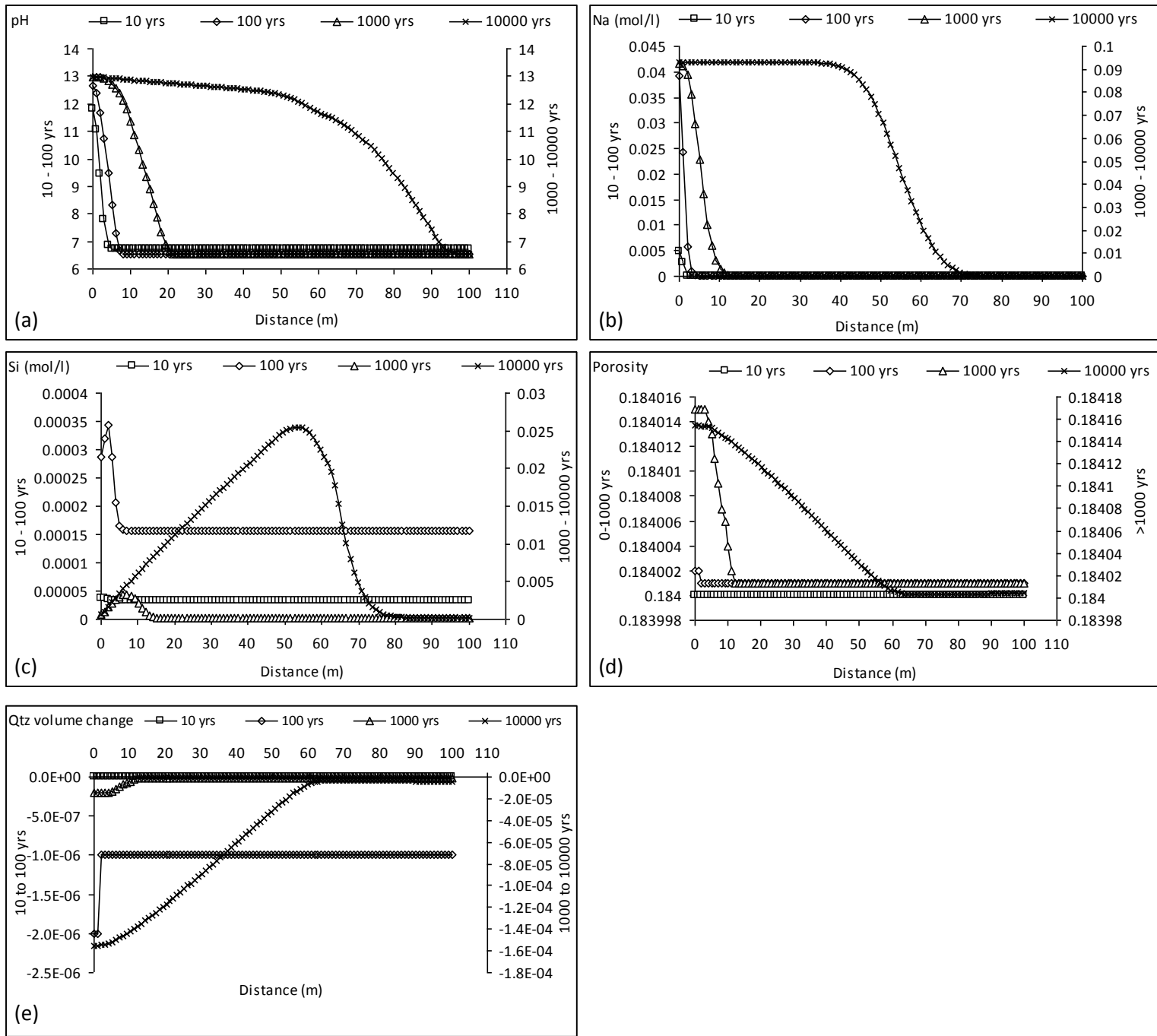
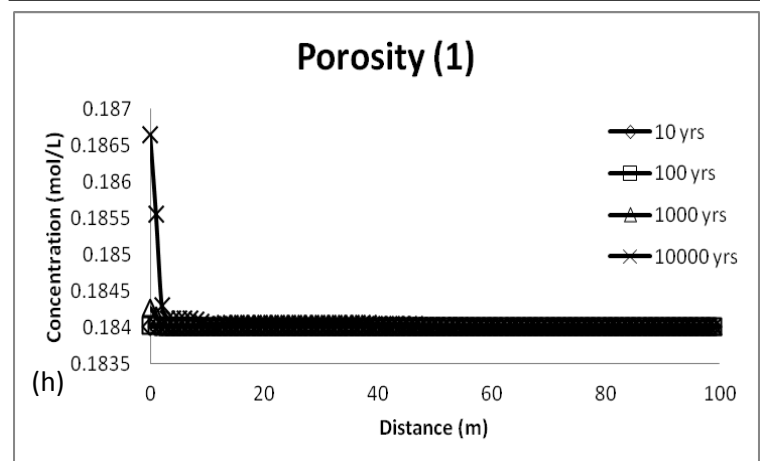
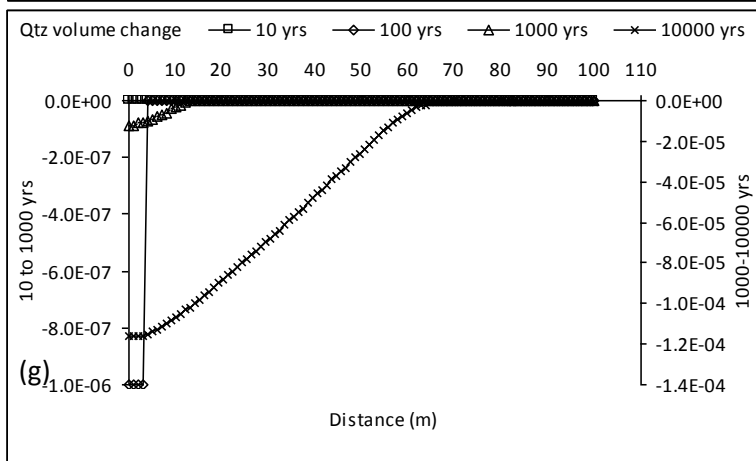
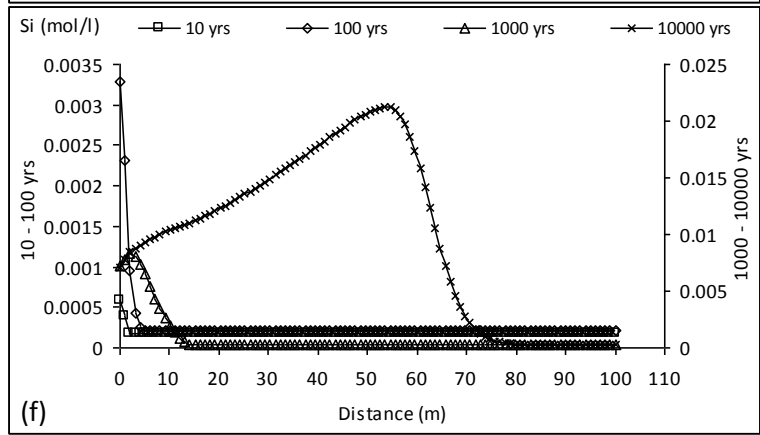
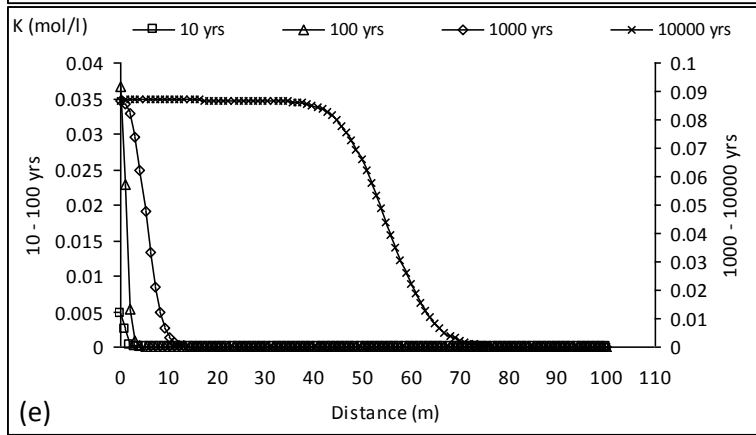
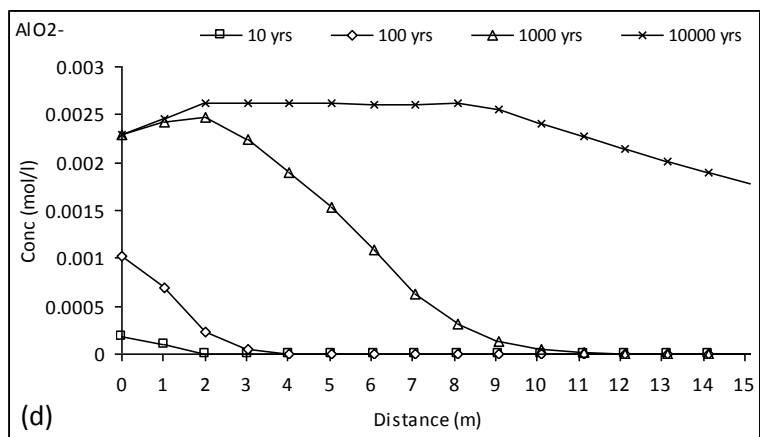
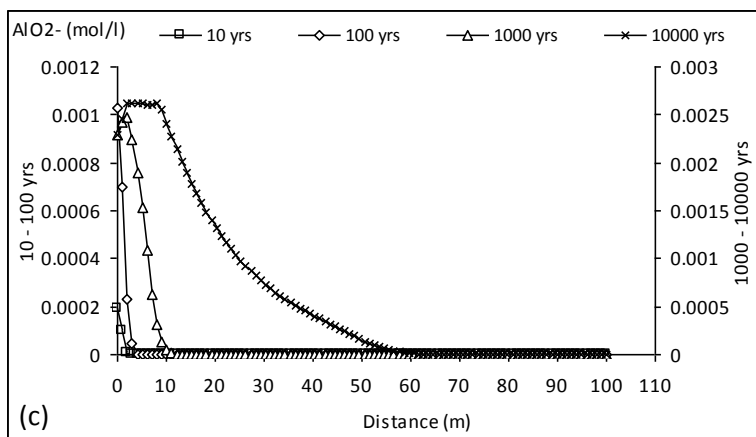
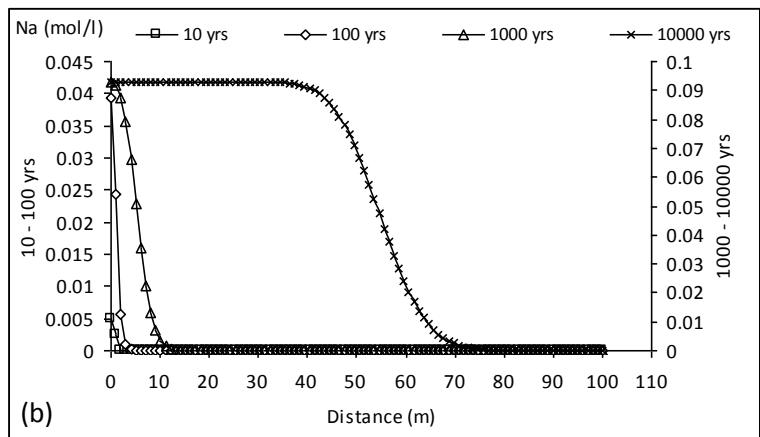
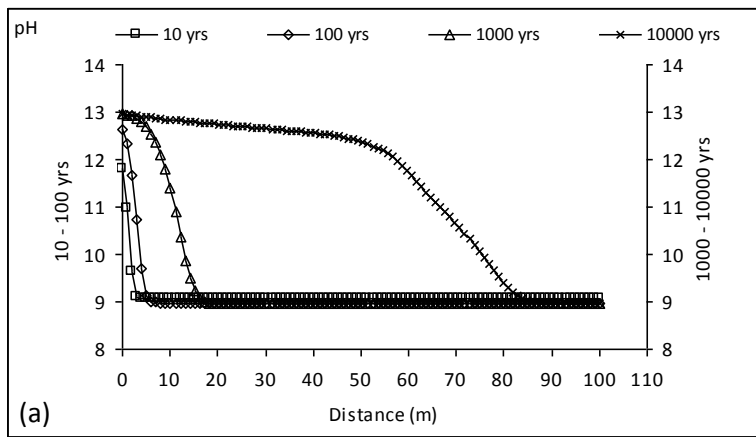
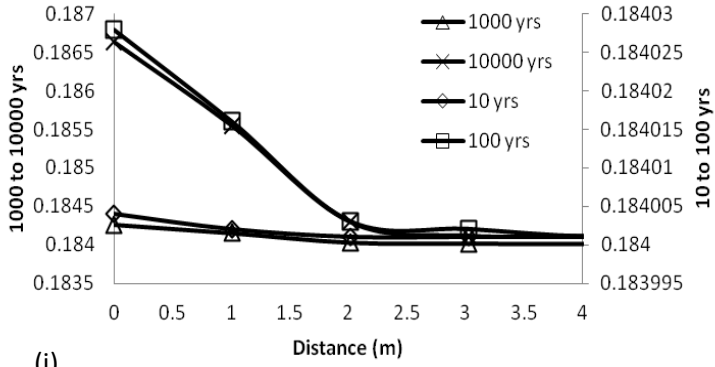


Figure 3. Predicted temporal variation in chemical and physical parameters with distance during migration of Young Cement Leachate through host rock composed of quartz only: (a) pH; (b) Na; (c) Si; (d) porosity distribution; (e) quartz volume changes.

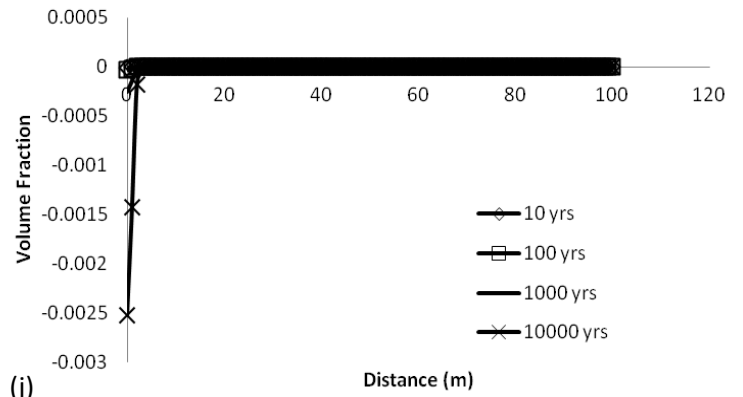


Porosity (2)



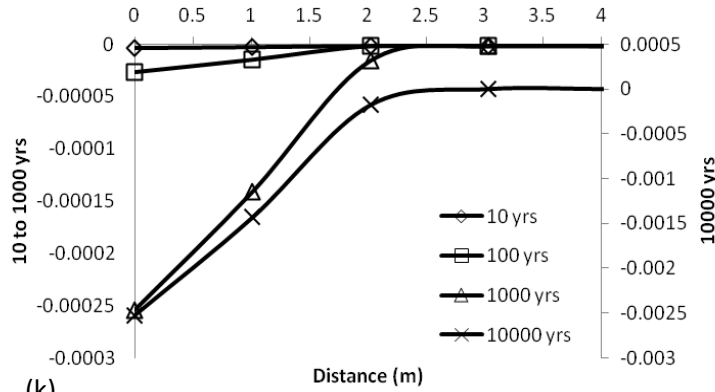
(i)

K-feldspar



(j)

K-feldspar volume shrink



(k)

Figure 4. Predicted temporal variation in chemical and physical parameters with distance during migration of Young Cement Leachate through host rock composed of quartz and feldspar: (a) pH; (b) Na; (c) AlO_2 ; (d) AlO_2 in the near-field; (e) K; (f) Si; (g) quartz volume change; (h) overall porosity change; (i) overall porosity change in the near-field; (j) K-feldspar volume change; (k) K-feldspar volume change in the near-field

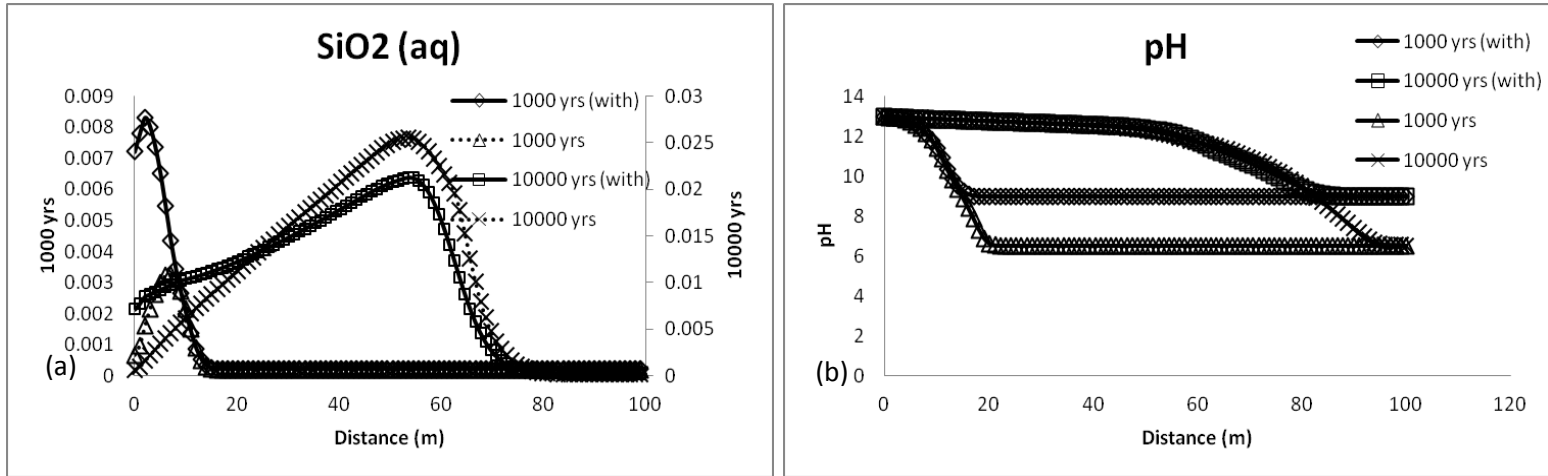
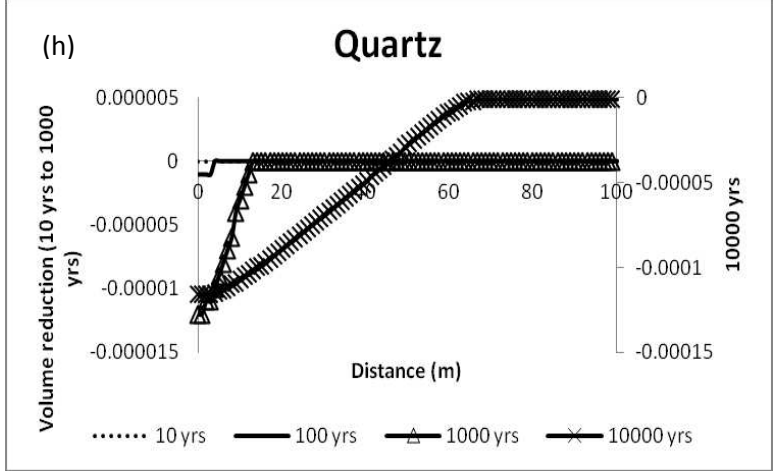
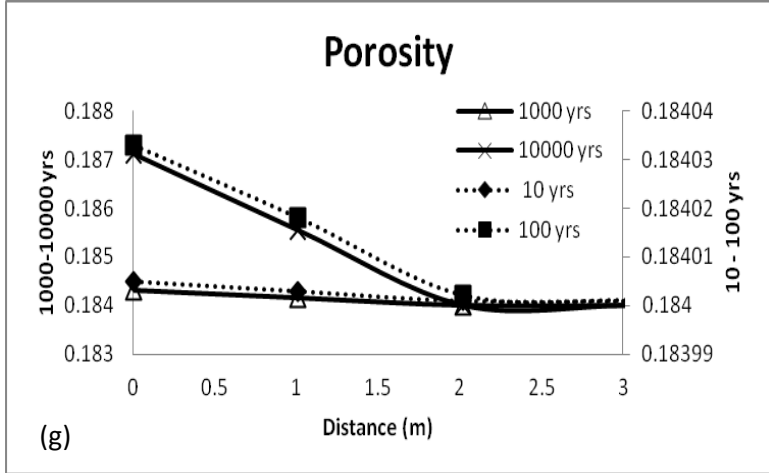
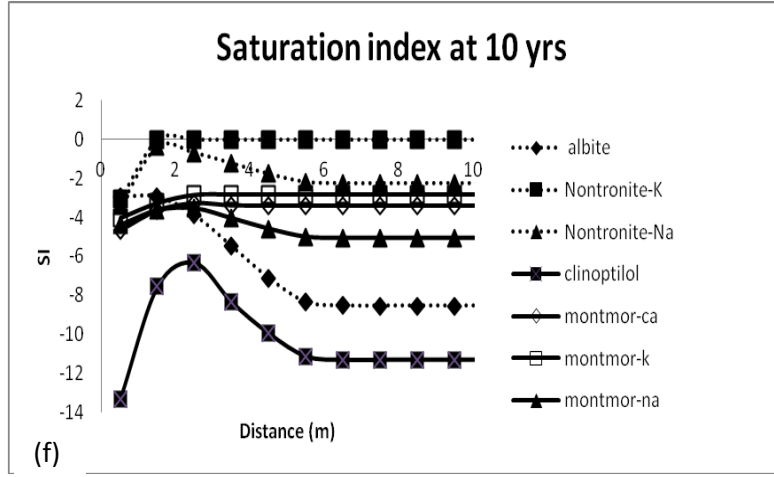
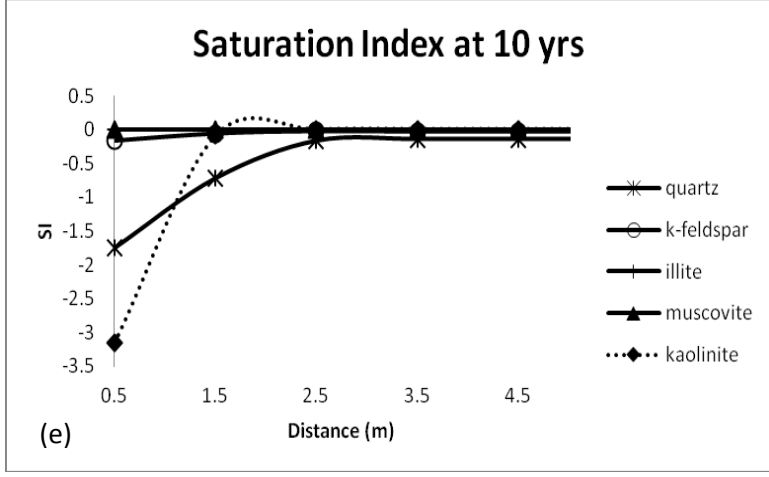
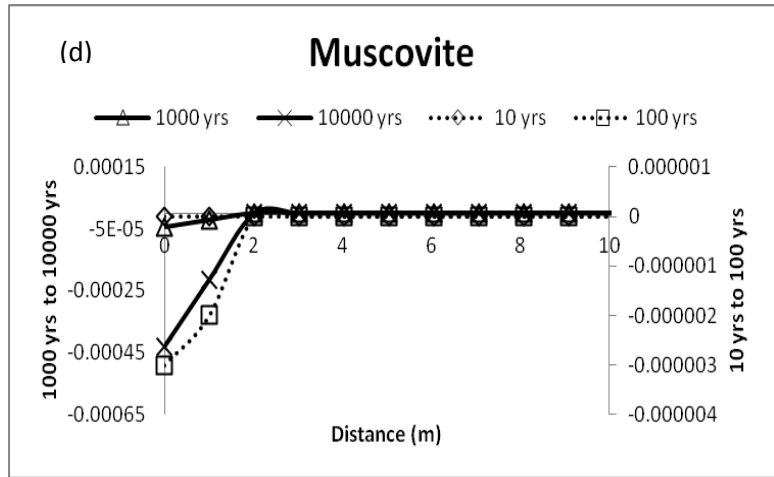
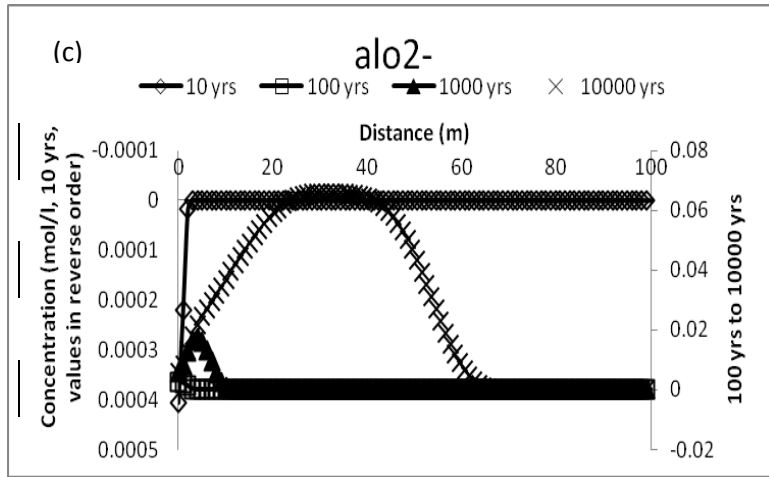
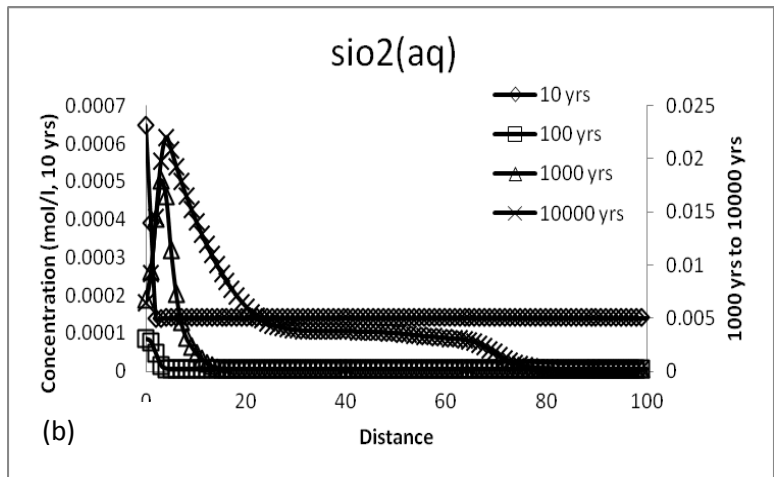
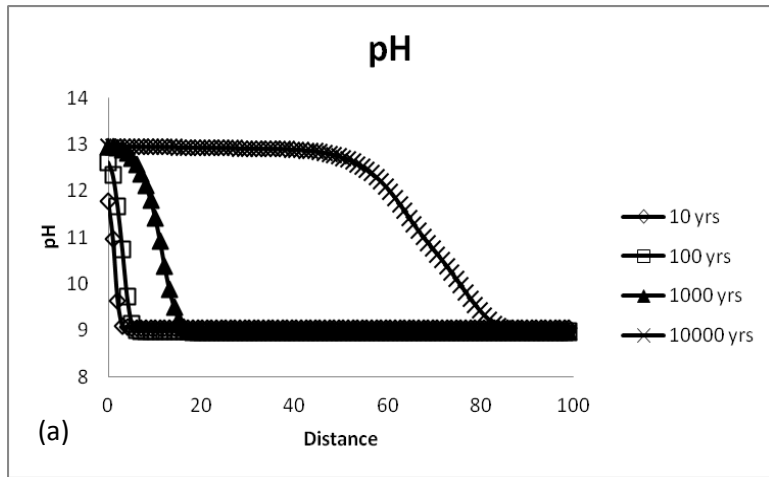


Figure 5. Comparison of scenarios for quartz only and quartz with k-feldspar: (a) SiO₂; (b) pH



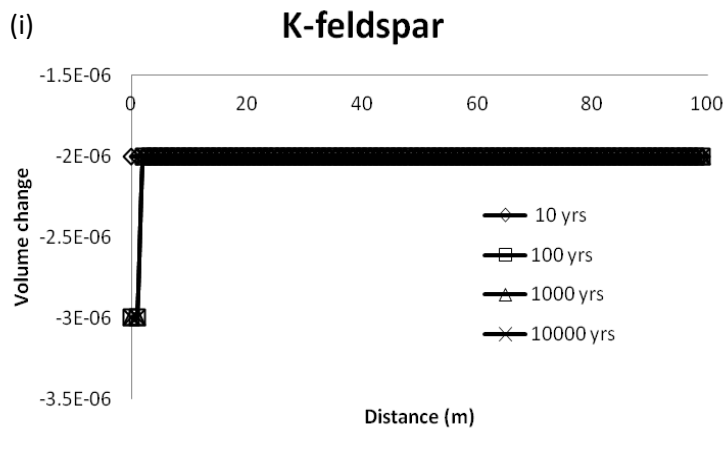


Figure 6. Predicted temporal variation in chemical and physical parameters with distance during migration of Young Cement Leachate through host rock composed of quartz, feldspar, illite, kaolinite and muscovite: (a) pH; (b) SiO₂; (c) AlO₂; (d) muscovite; (e) saturation indices; (f) saturation indices for near-field; (g) porosity; (h) quartz; (i) K-feldspar