Session 7A

Iron Clay Interactions
Chair: Reiner Dohrmann / Michel Cathelineau
EFFECTS OF TEMPERATURE, PH, IRON/CLAY RATIO AND LIQUID/CLAY RATIO ON THE CONVERSION OF DI-OCTAHEDRAL SMECTITE INTO IRON-RICH CLAYS: A REVIEW OF EXPERIMENTAL STUDIES

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Experimental conversion of the smectites to Fe-rich clay phases when in contact with iron metal and/or iron oxides was extensively investigated during the past decade (Guillaume et al., 2003, 2004; Perronnet, 2004; Charpentier et al., 2005; Lantenois et al., 2005; Wilson et al., 2005a, 2005b). These experiments simulated the mineralogical and chemical reaction of bentonites in contact with steel in high level nuclear waste repository. The compilation of available literature data shows that rather distinct mineral changes and sequences are observed in relation with the experimental conditions such as temperature, pH, iron/clay and liquid/clay ratios. To set up a conceptual model of the main mineralogical evolution, the role of physical-chemical parameters have to be considered and compared. It results that most changes of the mineralogical sequences may be attributed to distinct liquid/clay and iron/clay ratios used in experiments. In most of studies, redox conditions are low (from hematite-magnetite down that of dissociation of water) and experiments are carried out under a Ar or N₂ atmosphere. The main mineral sequences are the followings:

80°C < Temperature < 150°C and pH > 7:
- di-octahedral smectite (di-Sm) > 7 Å clay (berthierine, cronstedtite…) for iron/clay ratios > 0.5 and liquid/clay ratio > 10. Magnetite is a common by-product.
- di-Sm > Fe-di-Sm for iron/clay ratios < 0.5 and liquid/clay ratios < 10.

T > 150°C (250°C and 300°C experiments):
- di-octahedral smectite (di-Sm) > Fe rich saponite > tri-octahedral chloride + feldspar + zeolite (near neutral pH)
- di-Sm > Fe rich vermiculite + mordenite (high pH).

Low temperatures as well as high liquid/clay and high iron/clay ratios seem to be favourable conditions to crystallize clays of the serpentine group minerals. However, the prediction of the compacted smectite conversion in the presence of steel container is made difficult by the consideration of the temperature range of the processes (from 90°C down to 25°C) and the water/bentonite ratio (<0.2), in the repository. Under
these conditions, mineralogical changes may be rather hard to analyse quantitatively from experimental products carried out during short durations because of the slow kinetics of transformation. In addition, the determination of the nature of the Fe-Al-Si phases (berthierine, chlorite or Fe-saponite) at low temperature (80-100°C) and low fO₂ is very difficult because of analytical difficulties (very low amounts of newly-formed phases, same composition for berthierine and chamosite, almost similar X-Ray Diffraction patterns, 7 Å distances determination using HR-TEM may be due to interference fringes for 14Å phases, …). Using the reaction-transport code CRUNCH, Bildstein et al. (2006) predict the formation of serpentinelike phases at low temperature (50°C) but logarithmic activity diagrams suggest also that if pore waters are supersaturated or saturated with respect to magnetite, Fe(II)-rich saponite or berthierine may be alternately the dominant run products and mainly depend on fO₂ value and Fe³⁺/(H⁺)² ratios (Wilson et al., 2006³, 2006⁴).

The main challenges and questions for a full understanding of the iron canister/clay interface are the extrapolation of results: i) to conditions where water/rock ratio is lower than 0.5, for which the fluid chemistry is buffered by clays, a condition significantly different to that of most experiments already carried out; ii) from high T°C experiment to low T°C experiment. iii) The role of pCO₂, especially on the formation of Fe-carbonates has also to be considered as the exact value of pCO₂ is still debated and the renewing of CO₂ by diffusion is not fully known. iv) The role of iron metal-clay contact on mineral changes was evoked by Perronnet (2004) but not fully elucidated. v) Finally, iron passivation has been suggested and could be responsible to a reaction front depending on the diffusion of H₂ and Fe³⁺ in the solution, this yielding to a layer type alteration of the barrier or eventually a break in the formation of the run products, this needing still confirmation.

References:
MODELLING IRON-BENTONITE INTERACTIONS

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The presence of both iron canisters and bentonitic clay in some EBS designs for the geological disposal of HLW creates the potential for chemical interactions which may impact upon the long-term performance of the clay as a barrier to radionuclide migration. Flooding of potential radionuclide sorption sites on the clay by ferrous ions and conversion of clay to non-swelling sheet silicates (e.g. berthierine) are two possible outcomes deleterious to long-term performance.

Laboratory experimental studies of the corrosion of iron in clay show that corrosion product layers are generally thin (< 1 µm) with magnetite, siderite, or ‘green rust’ occurring depending upon temperature and ambient $PCO_2$. Experimental data from Smart et al. (in press) have shown that these alteration products buffer Fe$^{3+}$ ion concentrations at the iron-bentonite surface which act as a driver for Fe$^{2+}$ diffusion through, and sorption on, the bentonite (Charlet and Tournassat, 2005). In theory, incorporation of iron into clay alteration products could act as a ‘pump’ to accelerate corrosion.

However, the results of ‘mineralogical experiments’ to characterise the products of iron-bentonite interaction are less than unequivocal. The type and amounts of solid products appear to be strong functions of time, temperature, water/clay ratio, and clay and pore fluid compositions. For example, the products of high temperature experiments (> 250 °C) are dominated by chlorite (Cathelineau et al., 2005), whereas lower temperatures produce berthierine, odinite, cronstedtite, or Fe-rich smectite (Lantenois et al., 2005; Wilson et al., 2006). Unfortunately, the inevitable short-term nature of laboratory experimental studies introduces issues of metastability and kinetics. The sequential formation in time of minerals in natural systems often produces the formation of phases not predicted by equilibrium thermodynamics.

It is likely that the sequence of alteration of bentonite by Fe-rich fluids will proceed via an Ostwald step sequence. Although natural systems evidence is not completely analogous to waste package corrosion scenarios (there are no natural occurrences of carbon steel, for example), the low-temperature diagenesis of iron-rich sedimentary rocks shows that chlorite is the common Fe-silicate in ancient sandstones, but does not occur in recent sediments (< 1 m.a.), whereas the mixed ferrous-ferric silicates, odinite and cronstedtite occur in recent, shallow (< 60 m), warm (> 20 °C) tropical sediments (Odin, 1990), but do not occur in ancient sediments (> 1 m.a.). It may be concluded that although chlorite is the most likely stable Fe-silicate phase, its formation is kinetically inhibited, and occurs through an Ostwald step process via odinite, cronstedtite, and/or berthierine precursors.

The computer code QPAC-EBS has been modified to incorporate processes of nucleation, growth, precursor cannibalisation, and Ostwald ripening (e.g. Steefel and Van Cappellen, 1990) to address the issues of the slow growth of bentonite alteration products. This, together with incorporation of processes of iron corrosion, diffusion and sorption of Fe$^{3+}$ ions in the iron-bentonite system in the model has enabled the extrapolation of the results of short-term corrosion experiments to the long-term. Results and implications of this modelling both to the interpretation of short-term corrosion experiments and the prediction of long-term mineral alteration will be discussed.

References
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Charlet, L., and Tournassat, C., 2005, Fe(II)-Na(I)-Ca(II) cation exchange on montmorillonite in chloride medium: evidence for preferential clay adsorption of chloride - metal ion pairs in seawater: Aquatic Geochemistry, v. 11, p. 115-137.


IMPACT OF IRON ON THE BENTONITE BUFFER WITHIN THE KBS-3H DISPOSAL CONCEPT: RESULTS FROM REACTIVE TRANSPORT MODELLING

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INTRODUCTION AND OBJECTIVES

Steel components are unstable in EBS environments. They will corrode to fairly insoluble corrosion products, such as magnetite, and also react with the smectitic matrix of the bentonite buffer. The latter reaction process, referred here as iron-bentonite interactions, may involve different processes including sorption, redox and dissolution/precipitation reactions, the details of which are not yet understood. The process of greatest relevance for the buffer’s performance is montmorillonite transformation in contact with reduced iron. This process is a very slow and experimentally difficult to investigate. Current data (e.g. Guillaume et al., 2003; 2004; Wilson et al., 2006) suggest that the transformation process may either lead to a Fe-rich smectite (e.g. saponite) or to a non-swelling clay such as berthierine or chlorite. In addition, cementation effects resulting from precipitation of iron corrosion products or of SiO₂ induced by montmorillonite transformation need to be considered.

In the KBS-3H (horizontal) disposal concept, which is being developed by SKB and Posiva, prefabricated modules of spent fuel copper-iron canisters surrounded by bentonite blocks and an outer thin perforated steel supercontainer (SC) are emplaced in horizontal tunnels. Upon tunnel closure, groundwater from the granitic host rock will saturate the buffer material by swelling, both inside and outside of the SC, which is expected to induce an effective seal around the canisters. On the other hand, corrosion processes leading to significant quantities of oxidized iron species and hydrogen will occur. A key question is whether the released iron may affect the barrier performance of the buffer. In a preliminary study, this question was addressed with a very simple geochemical model using the Olkiluoto site as test case (Wersin et al., 2005). The results thereof indicated that the effect of the SC on the buffer was not significant. However, because of the non-consideration of clay mineral transformation reactions, no conclusions on the extent of the alteration zone could be drawn.

In this contribution, we present the outcome of a follow-up study in which the impact of the SC on the bentonite was assessed with a reactive transport modelling approach. The interaction of the corroding iron source with the bentonite matrix was simulated with a 1D diffusion-reaction model with aid of the geochemical codes PHREEQC and CrunchFlow. The Fe-bentonite interaction process included both Fe(II) sorption and dissolution/precipitation reactions of clay mineral phases which were based on carefully evaluated thermodynamic and kinetic data. A number of limiting test cases were run to explore the sensitivity of the results to uncertainties in data and model assumptions.

RESULTS AND CONCLUSIONS

The modelling results indicate that the flux of Fe into the buffer will be small and the extent of the buffer zone affected by iron-bentonite interaction processes will be limited. The largest Fe flux would arise from a relatively soluble FeCO₃ source and concomitant low Fe(II) activity in the porewater of the unaltered buffer. But even for this case and time scales of 10⁶ years, no large detrimental effect on the buffer were predicted. This is illustrated in Fig. 1 for a limiting test case with a high montmorillonite solubility, which shows the mineral volume fraction after 10⁶ and 5·10⁴ years.
Figure 1: Mineral distribution for a typical test for $5 \times 10^5$ years (solid lines) and $10^5$ years (hatched lines).

It should be noted that the uncertainties in the underlying thermodynamic and kinetic data and in the description of solute diffusion are rather large.

In conclusion, this reactive transport modelling study indicates that for the KBS-3H design adverse effects on the swelling buffer material may occur due to interaction between the supercontainer iron and bentonite, but that these will be spatially limited to the outermost few cm near the buffer-supercontainer-rock interface for very long time periods. This is mainly because of (i) the limited Fe(II) gradient between the Fe source and the undisturbed bentonite, (ii) the strong retention of Fe(II) by the clay surfaces and (iii) clogging effects resulting from precipitation of corrosion products and Fe-rich clay such as berthierine. This physically affected area close to the supercontainer, however needs to be considered in performance assessment calculations.

References


CHARACTERIZATION OF A REDOX-MODIFIED CLAY MINERAL WITH RESPECT TO ITS SUITABILITY AS A BARRIER IN RADIOACTIVE WASTE CONFINEMENT

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INTRODUCTION
Engineered barriers for high-level nuclear waste (HLW) consist of excavated repositories in sub-surface rock formations where canisters holding the radionuclide are stored. Clay minerals, particularly the 2:1 swelling types, are used as backfill material both in the canisters and in the bore hole in order to prevent radionuclide transport to surrounding groundwater. One of the most important processes that can occur is the corrosion of the canister that could be coupled with reduction of iron (Fe) in the clay structure. Such changes would greatly decrease the long-term stability of the clay and, consequently, of the barriers themselves. A clay mineral material from a commercial source located in the Kutch region, India, is one candidate to serve as such a barrier material. The purpose of the present study was to evaluate its performance and stability under variable redox conditions.

EXPERIMENTAL CONCEPT
The unaltered clay was characterized by X-ray diffractometry (XRD) of both random- and parallel-oriented samples and of samples which were Mg saturated and ethylene-glycol solvated; by thermal analysis (TGA/DTGA); by Fourier-transform infrared (FTIR) spectroscopy; and by variable-temperature Mössbauer spectroscopy. The chemically reduced clay was prepared by adding 150 mg of sodium dithionite to 30 mg of clay in citrate-bicarbonate buffered aqueous suspension under N₂ flow for 4 h at 70°C (Stucki et al., 1984). The reduced clay was reoxidized by bubbling O₂ through the suspension for 24 h at room temperature. These reduced and reduced-reoxidized forms of the clay were then analyzed by Mössbauer spectroscopy at 298, 77, and 4 K and analyzed chemically for Fe(II) and total Fe using the 1,10-phenanthroline method of Komadel and Stucki, (1988).

RESULTS AND INTERPRETATION
In the unaltered state the multiple techniques indicated that the clay is comprised of smectite (determined by XRD), maghemite, superparamagnetic goethite, and hematite (determined by Mössbauer spectroscopy)

![Figure 1: Mössbauer spectra at 4 K of (a) unaltered, (b) reduced, and (c) reoxidized Kutch Clay.](image-url)
and a minor amount of kaolinite (determined by FTIR spectroscopy). The reduction treatment should have removed all Fe (oxyhydr)oxides from the sample, but even after this treatment a small magnetically ordered (sextet) phase persisted in the Mössbauer spectrum. One possible explanation for this persistent sextet is that a portion of the maghemite resisted the reductive dissolution treatment. A more likely explanation, however, is that the introduction of some Fe(II) into the clay structure induced some magnetic order of structural Fe, which is consistent with observations of Lear and Stucki (1987). Upon reoxidation no six-line pattern was observed, indicating that Fe is present only in the structure of the silicates or in small clusters. The final structure of the reduced-reoxidized clay contained more defects than the original clay, as revealed by greater quadrupole splitting values for structural Fe(III) in the clay. These findings indicate that upon exposure to natural redox cycles, the Kutch clay could undergo permanent changes in its mineralogical composition and clay mineral structure. Further study is required, however, to ascertain the effects that such changes would have on its long-term stability as a barrier material. Suggested future measurements include effects of multiple redox cycles on cation exchange capacity, swelling pressure, hydraulic conductivity, and crystal structure. Changes in these properties to various degrees are expected in any Fe-bearing smectite subjected to redox cycling.

References:
