

**R-08-45**

**Impact of iron on the  
performance of clay barriers  
in waste disposal systems**

**Report on the status of research  
and development**

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May 2008

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This report concerns a study which was conducted for SKB. The conclusions and viewpoints presented in the report are those of the authors and do not necessarily coincide with those of the client.

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# Abstract

The interaction of iron components with swelling clay materials in the EBS has received relatively little attention so far in safety assessment studies. It is however widely recognised that such interaction processes (e.g. corrosion, mineral alteration) need to be considered since they have the potential to impair repository long-term safety.

A workshop on this topic was held in 2006 in Basel (Switzerland) and has shed some light on the current status and the remaining uncertainties of relevance for safety purposes. Also, the workshop highlighted that there is strong interest to continue research in this field. Notably, waste management organisations from France, Finland, Japan, Sweden and Switzerland showed interest to exchange information in this research area on a regular basis and, if possible, advance common projects.

Following this workshop, it was decided by Posiva, SKB and Nagra to compile the status of research and development based on a pre-formatted questionnaire sent out to a number of research organisations. This report summarises the information obtained. This serves to identify the remaining knowledge gaps and to explore areas of common interest. Some ideas for common research studies and possibilities how to organise these are presented.

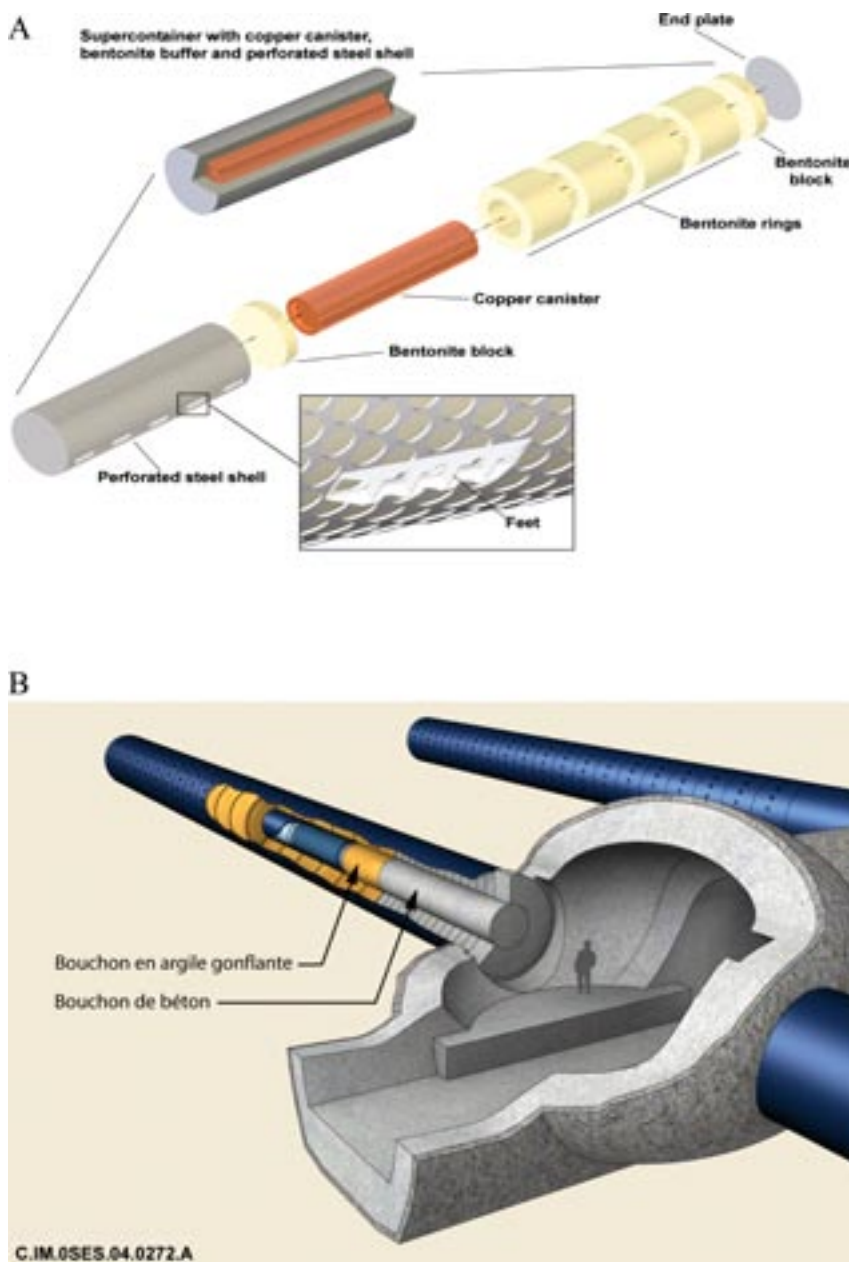
This report has been published also as an SKB report, SKB R-08-45.

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# 1 Introduction

Virtually all high-level waste repository concepts contain iron components. Thus, steel canisters with or without a copper shell constitute an essential part of the EBS in most European concepts. A lesser fraction of iron is present as rails, anchors or rock bolts. In addition, a further large steel component, the “supercontainer” in the KBS-3H concept and the “steel sleeve” French 2005 concept for spent fuel disposal, is envisioned at the interface between the buffer and the host rock (see Figure 1-1).



*Figure 1-1. Schematic views of KBS-3H (A) and French EBS for spent fuel (B) concepts.*

The iron in the EBS will interact via the corrosion process with the swelling clay (bentonite or crushed claystone) foreseen as buffer and plug material or with the clay matrix of the host rock, for example in the case of the French disposal concept. This interaction may, in principle, affect the properties of the clay, e.g. affect its sealing properties by mineral alteration.

The iron-clay interaction processes and their effects on repository safety have received little attention in past. Only recently, the need for research in this area has been recognised and some research programs have been initiated. A milestone in this regard was the workshop on Fe-clay interactions in repository environments (launched by Andra, SKB and Nagra) that took place in Basel, Switzerland in May of 2006 /Wersin and Mettler 2006/. Based on the outcome of this workshop and also due to the specific interest raised within the KBS-3H concept study, we decided to compile the status on the research and development in the field of Fe-clay interactions. This was done by sending a pre-formatted questionnaire to a number of research teams, also including those not involved in radwaste programs. The research organisations contacted were selected in an arbitrary fashion. Thus, the questionnaire was sent out to all organisations participating at the Basel workshop in May 2006 and to several other European research teams who have published work on the Fe-clay topic. A list of the participating organisations (including abbreviations) is given in Appendix A. The information obtained from the questionnaires should serve as basis for creating (a) common new research proposal(s) supported by waste management organisations.

This report first briefly summarises the outcome of the workshop and then presents the status of research derived from the input (via the questionnaires) of the research organisations. Thereof, some ideas for continuing research work in this field are presented.

## 2 Key issues to address

Steel components are unstable in EBS environments. They will corrode to more oxidized corrosion products, such as magnetite, and react with the adjacent clay materials. These processes are interlinked and thus the Fe-clay interactions cannot be fully understood without considering corrosion of the starting zero-valent Fe material. Anoxic corrosion of Fe components produces large amounts of H<sub>2</sub>, which generally is regarded as inert, and thus not considered in Fe-clay interactions. However, this assumption still awaits experimental verification. The generation of large amounts of gas is though considered in the evaluation of the eventual formation of gas overpressure e.g. in tight drift sections in the emplacement tunnels.

From the safety perspective, Fe-clay interactions call for a number of questions to be resolved, such as:

- What is the fate of corroded iron, i.e. which is the proportion which will end up in corrosion products and which one in the clay?
- Related to the first question is the extent of alteration of the swelling clay fraction (i.e. smectite) to a non-swelling Fe-rich clay with time. Which are the thermodynamic and kinetic constraints for this transformation process?
- How does sorption of Fe(II) (released by corrosion) to the clay surface affect the sorption properties of the clay. Or, in other words, is there competition between Fe(II) and radionuclides for sorption sites?
- Dioctahedral smectites contain a significant fraction of structural Fe(III). Does the interaction with the corroding Fe from the canister lead to reduction of this Fe(III)? If yes, how does this affect swelling and hydraulic properties?
- Does hydrogen produced by corrosion have to be considered in the Fe-clay interaction processes?

### **3 Summary of the Fe-bentonite workshop, May 2006**

The workshop included the four sessions: (I) treatment of Fe-clay interactions in the safety case, (II) corrosion phenomena in clay media, (III) chemical mechanisms of Fe-clay interactions, and (IV) transport of Fe and impact on buffer material.

The outcome from session I was: The effects on Fe-clay interactions have only been very crudely considered in the safety assessments of SKB and Nagra. On the other hand, Andra put quite a lot of emphasis on including potential effects of Fe-clay interactions in their Dossier 2005 assessment, but, due to the preliminary nature of the studies and large conceptual uncertainties, such effects could not be treated in detail. It was concluded however, that, (1) because of potential detrimental effects the amount of iron should be reduced in further EBS designs and (2) that research on specific issues should be continued.

Concerning corrosion (session II), the knowledge on processes in repository systems is relatively good. Anoxic corrosion rates of steel in compacted bentonite show a strong decrease with time due to the build up of a protective oxide film. However, uncertainties still persist in the corrosion rates of long timescales and with regard to the nature of the corrosion product. This also arises in uncertainties in the Fe concentration at the source, which needs to be considered in coupled diffusion-reaction calculations.

The central topic was on the finding from experimental Fe-clay interaction data (session III). The work can be separated in sorption and alteration studies. The outcome of both types of studies showed that large uncertainties still persist in the understanding of the underlying processes. In terms of sorption data, it could be shown that sorption of Fe(II) to montmorillonite is very strong at near-neutral to alkaline conditions and appears to involve a combined redox and co-precipitation reaction rather than a simple surface complexation reaction. The alteration data suggest that there are mainly two pathways for smectite transformation in contact with reduced Fe: (1) transformation to an Fe-rich smectite of higher layer charge (Fe-rich saponite, nontronite) and (2) transformation to a non-swelling Fe clay, such as Fe-serpentine (berthierine, cronstedtite) at lower temperatures and chlorites (e.g. chamosite) at higher temperatures. The uncertainties on the thermodynamics of these newly formed phases and on the transformation kinetics are still large.

In session (IV), the results from modelling exercises were presented which were based on coupled diffusion-chemical reaction calculations. The uncertainties in process understanding were obviously also reflected in the modelling results. Nevertheless, the coupled approach allowed constraining the effect of Fe-clay interaction within reasonable limits. The results from three quite different modelling studies indicated that the alteration of the swelling clay would be spatially limited for very long times, because of the diffusional constraint and the clogging effects resulting from neo-formations. Within the same session, preliminary data on physical effects induced by Fe-bentonite interactions were reported. These data suggested that no notable effects on swelling pressures, but rather significant ones on hydraulic conductivity had occurred. This could have been induced by cementation effects, but it was not clear which type of “cement” could have formed.



From the final discussion session, the following conclusions could be drawn:

- The perhaps most serious gap of knowledge from a safety perspective regards the physical properties of Fe-exposed bentonites. Thus, an effort to gain more experimental data and interpret geochemical and mineralogical data in the light of swelling pressure and hydraulic conductivity is urgently needed.
- There is little natural analogue data available. Analysis of ancient iron objects buried in clay sediments or Fe-rich altered volcanic rocks might provide interesting information.
- Preliminary modelling data point to a spatially limited influence of Fe-smectite interaction. More advanced coupled reactive transport models offer a good perspective to help to constrain the problem for safety assessment purposes.
- The relevance of Fe-smectite interaction strongly depends on repository design, i.e. on the geochemical and transport conditions in the host rock, the amount of iron components and the mass ratio between iron and adjacent bentonite material.

## 4 Outcome of questionnaires and other information

### 4.1 Status of research

The research work on iron-clay systems is presented in the sub-areas “corrosion”, “sorption”, “mineralogical alteration” and “modelling”. It should be noted however, that this separation is somewhat artificial since many studies address two to three sub-areas. Information presented is principally derived from the questionnaires which are listed in Appendix B.

#### 4.1.1 Corrosion

##### ***CEA Cadarache (F)***

Steel coupons in compacted FoCa7 bentonite were contacted with “in situ” granite water in a percolation scheme at a high hydrostatic pressure of 30 bars. The experiments were performed at 25 and 80°C for a period of 6–8 months under anoxic conditions. The main results were: (1) uniform corrosion at 25°C with rates of 4 µm/a, and heterogeneous pitting corrosion at 80°C with an averaged rate of about 5 µm/a. The main corrosion product was magnetite, but minor transformation of bentonite into berthierine was also identified. In addition, at the Fe-clay interface, calcite precipitation and minor siderite and green rust were observed. The original smectite and quartz showed signs of alteration. The work was performed during 1997–2002 and is completed now. The results are documented in /Papillon et al. 1999, 2003/.

##### ***Nuclear Research Institute - NRI (CZ)***

The first type of work involves electrochemical studies with iron powder and carbon steel electrodes contacted with artificial bentonite water in corrosion cells at different temperatures under N<sub>2</sub> atmosphere. Corrosion rates are determined. Later on Rokle bentonite will be included and corrosion rates will be compared with bentonite-free experiments. The work started in 2005 and will last till 2008. Only preliminary results are available which are documented in a RAWRA report and in /Vokal et al. 2006a/.

In the second study, the corrosion and diffusion of Fe in compacted Rokle bentonite is investigated. Iron powder is brought in contact with saturated bentonite at different densities and temperatures up to 80°C in a diffusion setup (under N<sub>2</sub> atmosphere) The study started in 2004 and will last till 2008. It is planned to also determine swelling pressures of exposed samples. The work is documented in a RAWRA working report and in /Vokal et al. 2006ab/. Only rather preliminary data are available to date.

The third study which represents the continuation of the second one will focus on the diffusion of Fe and the effect of iron and iron corrosion products on the sorption of selected radionuclides (under N<sub>2</sub> atmosphere). This study will start this year and terminate in 2008. Some preparatory laboratory work on sorption and diffusion of Cs has been published /Vesjada 2006, Vesjada et al. 2006/.

##### ***Sercos Assurance (UK)***

In a combined long-term study, supported by SKB and NF-PRO, iron materials (carbon, cast and stainless steels) and compacted MX-80 bentonite have been contacted with artificial groundwaters for various periods (up to 30 months) under anaerobic conditions. The main focus is on corrosion aspects (rates, products), but part of the study has been done in collaboration with other organisations (e.g. Clay Technology) to determine the physico-chemical effects on bentonite induced by corrosion-related phenomena (see study by Posiva/SKB below). The work started in 2001 and is still ongoing. The corrosion part of the work has been published in /Smart et al. 2004/, the iron-bentonite interaction work in /Carlson et al. 2007 and Smart et al. 2006/.

### **CEA Saclay (F)**

Corrosion studies in compacted bentonite and Callovo-Oxfordian claystone (argillite) have been performed /e.g. Bataillon 2006/. In the case of bentonite, high swelling pressures and, in general constant pCO<sub>2</sub> conditions were applied. The long-term corrosion data showed an averaged rate of 3 µm/a and a protective film composed of a thin magnetite and thick siderite layer. In the case of the argillite experiments, more complex corrosion products and iron phyllosilicate phases were observed.

## **4.1.2 Mineralogical alteration and characterisation**

### **BGR (G)**

As part of the “Ideal Bentonite” project, the effect of iron or “corrosivity” on a variety of bentonite materials in the form of powders or gels is being tested. The goal is to determine the bentonite which is least altered by Fe-bentonite interactions. The project started in 2002 and will last until 2010. It is planned to expose bentonite materials to Fe(II) chloride solution in the near future. Preliminary data has been presented as poster at the Tours conference in 2005 /Kaufhold and Dohrmann 2005/.

### **BRGM (F)**

The main focus in this research area is on the speciation of Fe and the definition of the redox state in clay formations. For this purpose, a rigorous experimental protocol extracting Fe minerals under anaerobic conditions is applied. The different solid iron species are analyzed by spectroscopic methods, such as Mössbauer spectroscopy. Dissolved iron is also determined and serves as input value for different modelling exercises /Gaucher et al. 2006/. This work is partly performed within the EC-project FUNMIG. This team is also preparing a thermodynamic database for clays /e.g. Gailhanou 2006/.

The research group has an ongoing collaboration with the University of Grenoble on the sorption and redox reactions between Fe(II) and smectites (see section 4.1.4). A topic which the groups intend to focus on is on the chemistry of iron at the interface between cement and clay.

### **CEA Cadarache (F)**

An experimental study, in which FoCa7 bentonite - iron powder suspensions under N<sub>2</sub> atmosphere up to 150°C were reacted in batch-type systems, was performed in 2001–2004. The focus was to investigate mineralogical and geochemical effects induced by this interaction process. The main corrosion product identified was a Fe-rich serpentine. This was accompanied by a strong decrease in CEC. The work is documented in /Perronnet 2004 and Perronnet et al. 2007/.

A further study involves the modelling of the Fe-clay interactions within the Andra disposal concept. A coupled reactive transport model has been applied. The work which was initiated in 2003 was scheduled to be terminated in 2007.

### **Clay Technology (S)**

The project on the interaction with the corrosion of iron wires and iron nails in compacted bentonite in collaboration with SKB, Posiva and Serco Assurance is mentioned above /Carlson et al. 2006/. Moreover, the effect of heating on three different bentonites (Czech, Indian, MX-80) with variable Fe content was tested /Karnland 2006/. The materials were heated up to 90°C for one year. The results indicated that no changes in swelling properties, hydraulic conductivity or cation exchange capacity had occurred for all samples. It was concluded that high contents of structural iron bentonite has no obvious effects with regard to sealing properties of bentonite.

At present, the ongoing long-term corrosion experiments performed at Serco Assurance are periodically being analyzed for their physical properties. This work was scheduled to be terminated in 2007 or 2008.

Clay Technology is also involved in the PhD of Daniel Svensson (SKB Äspö and University of Lund). The main focus therein is to analyse the effect of structural iron in bentonite with regard to the buffer's sealing properties.

### ***ETH Zurich (CH)***

The Clay Lab performed some research work in this area in the eighties and nineties, such as a mineralogical investigation of Fe-rich bentonites /Nagra 1986/, and experimental studies on the interaction of magnetite and Fe(0) with bentonite /Müller-Vonmoos et al. 1991/ and on Fe diffusion through compacted bentonite /Madsen and Kahr 1991/. At the moment, no new project is planned, but a pre-study on the corrosion mechanism of iron, copper and aluminium in contact with bentonite under anaerobic conditions has been performed.

### ***JAEA (J)***

Compacted Kunigel V1 bentonite and Fe coupons were contacted with synthetic seawater under a N<sub>2</sub> atmosphere at 80°C for a period of four years (1997–2001). A column scheme was used. The identified iron products after this reaction period were siderite and ankerite and exchanged Fe in the smectite interlayers. No neoformation of Fe silicates could be identified by XRD analysis. No change in swelling ability of the exposed bentonite was noted. The work is documented as conference abstract /Shibata et al. 2002/.

Another study involved hydrothermal experiments with Kunipia-F bentonite and 1 mol/l Fe(II) solutions at rather low solid/liquid ratios under N<sub>2</sub> atmosphere. The bentonite was exposed for 1 to max. 20 months at temperatures of 150 and 250°C. The final solutions had rather low pH values of 5.5–6.1. The results showed a decrease in CEC and an increase of Mg and a decrease of Fe exchanger cations. No clear clay alteration product could be identified, but XRD analysis suggested the appearance of minor amounts of non-expandable clay in samples exposed to 250°C. The study was conducted from 2004–2006. The work is documented in JAEA reports /Suyama et al. 2006, 2007 and Shibata et al. 2005/.

Thirdly, a long-term study on Fe-bentonite interaction, starting in 1996 and ending in 2007 is being performed. Compacted Kunigel bentonite/sand and iron coupons are being exposed to synthetic seawater at a temperature of 50–80°C. The experiments are performed in a nitrogen atmosphere in a column-type setup. The analytical work was scheduled to be performed in 2007.

### ***Posiva/SKB (FIN/S)***

Compacted MX-80 bentonite and iron materials (coupons, wires) were exposed to NaCl-Na<sub>2</sub>CO<sub>3</sub> solutions at 30 and 50°C under a nitrogen atmosphere in 2004–2006 (see also under Serco Assurance). A number of analytical methods were applied to analyse the solid materials. The identified corrosion products were hematite, goethite and magnetite. No newly formed Fe silicate could be identified. However, the iron content in the bentonite strongly increased, suggesting the formation of Fe phases. From the observed change in colour (blue-green), it was deduced that reduction of some structural iron had occurred. Analysis of physical properties indicated a significant increase in hydraulic conductivity, but virtually no change in swelling capability. The corrosion part of the work is presented above (under Serco Assurance). The work is documented in a Posiva Working Report /Carlson et al. 2006/ and in a paper /Carlson et al. 2007/.

A new study at the Äspö Hard Rock Laboratory within the Alternative Buffer Material (ABM) experiment is being performed. A number of different bentonite and other type of clays are contacting a heated iron surface and are being heated up to 130°C for a period of 1–5 years. The tests started at the end of last year.

### **Quintessa (GB)**

The interaction of Fe with bentonite is being assessed within the NF-PRO project (EU 6<sup>th</sup> framework programme). The goal is to perform a comprehensive modelling exercise including corrosion, Fe diffusion through bentonite and long-term alteration of the clay. Tests (modelling?) were successfully performed to simulate experimental data. The work also includes a literature survey and a review of natural systems. The study was scheduled for 2004–2007. The work will be documented in NF-PRO reports.

### **University of Bern (CH)**

So far, there has been no work related to Fe-clay interactions in the research group of Rock-Water Interactions. However, it is planned to get involved in natural analogue related to the alteration of smectites via illitisation and Fe-clay interactions. The second topic would involve a feasibility study where samples from various natural native Fe occurrences (especially those occurring in basaltic lava formations) studied in terms of Fe distribution and clay alteration effects.

### **University of Bristol (GB)**

The research team of Vala Ragnarsdottir performed a PhD study on the thermodynamic properties of Fe-rich clays /Wilson et al. 2006ab/. At the moment no new work on this topic is planned, but there is strong interest to continue research in this field.

### **University of Grenoble (F)**

The experimental study on Fe-bentonite interaction was presented at the workshop by B. Lanson. Part of this work is published in /Lantenois et al. 2005/. At the moment no project on this topic is ongoing, but there is an interest to collaborate in this research field.

### **University of Nancy (F)**

The research team of Michel Cathelineau has conducted several studies on the interaction of Fe phases with bentonite /Guillaume et al. 2003, 2004, Charpentier et al. 2006, Cathelineau et al. 2005, Cathelineau 2006/, generally at lower solid/liquid ratios and higher temperatures (80 to 300 °C). Depending on the conditions, different neo-formed clay phases, such as nontronite, saponite and berthierine were formed. Further experimental work on Fe-bentonite interactions is planned within the Andra's new research program "Glass-Iron-Clays".

## **4.1.3 Sorption**

### **PSI (CH)**

So far, no work on this topic has been performed. It is, however planned to quantify the effect of Fe(II) competition on the sorption of radionuclides in bentonite. The study will involve MX-80 bentonite and montmorillonite suspensions in Fe(II) solutions in a batch-type setup. The work is to begin this year. Besides classical wet chemistry analyses, XAS analysis on the solid materials will be performed.

### **University of Grenoble (F)**

The research team of Laurent Charlet has dedicated a number of studies on the interaction of Fe(II) with smectite minerals under anoxic conditions. This work included Fe(II) sorption to purified and Fe-free montmorillonite /Tournassat 2003, Charlet and Tournassat 2005, Géhin et al. 2007, Charlet 2006, Tournassat et al. 2007/. The ongoing work is performed in close collaboration with BRGM.

Further still ongoing work involves the study of the reactivity of Fe(II) in terms of reductive potential for redox sensitive radionuclides, such as selenium in clays /Charlet et al. 2007/ and corrosion products /Scheinost and Charlet 2007/ or uranium. Another aspect is the study of the effect of sorbed Fe(II) on the sorption of other metals, such as Eu(III) and Co(II). An interesting result is that, contrary to what might be expected, sorption of these elements is enhanced at high loadings of Fe(II).

#### ***PSI (CH)***

So far, no work on this topic has been performed. It is, however planned to quantify the effect of Fe(II) competition on the sorption of radionuclides in bentonite. The study will involve MX-80 bentonite and montmorillonite suspensions in Fe(II) solutions in a batch-type setup. The work is to begin this year. Besides classical wet chemistry analyses, XAS analysis on the solid materials will be performed.

#### **4.1.4 Modelling**

##### ***CEA Cadarache (F)***

A further study involves the modelling of the Fe-clay interactions within the Andra disposal concept. A coupled reactive transport model has been applied. The work that initiated in 2003 will be terminated this year. The results show that significant porosity reduction may occur at the steel-clay interface due to the precipitation of iron oxides (magnetite). In bentonite, the primary clay minerals are destabilized and iron-(alumino)silicates form. This work is documented in /Bildstein et al. 2006/.

##### ***Posiva/SKB/Nagra/Clay Technology***

The Fe-bentonite interactions within the framework of the KBS-3H disposal concept have been assessed by a literature survey and a modelling exercise using the Olkiluoto site as test case. For this sake, reactive transport calculations were performed in order to describe the movement of Fe from the supercontainer towards the inner part of the bentonite buffer and to estimate the amount of bentonite altered by Fe-clay interactions. The work initiated in 2005 and was terminated in 2007. It is documented in /Wersin et al. 2005/ and /Wersin et al. 2007/.

##### ***CGS (CNRS) at University Louis Pasteur of Strasbourg (F)***

A modelling study involving Fe-clay interaction processes in compacted MX-80 bentonite within the French repository concept was performed within two PhD studies /Sali 2003, Marty 2006/ during the period 2002–2005. The work was done in collaboration with research teams of the University of Nancy who provided experimental data. The mineral evolution due to corrosion and clay mineral transformation was simulated up to 100,000 years. The resulting main transformations predicted were illitization, saponitization and vermiculitization. The work has been published in various Andra reports and in /Montes-H et al. 2005abcd/.

A new project is planned within the Andra's new research program "Glass-Iron-Clays". It will involve a continuation of the simulation work in collaboration with the University of Nancy by developing a new geochemical code (NANOKIN) which specifically includes crystal growth processes.

#### **4.1.5 Summary of ongoing studies**

The studies that are running or have run until this year are listed in Table 4.1. It is of interest to note that quite a lot of new data can be expected this year from the NF-PRO- related work.

**Table 4.1. Summary of on-going studies.**

Research Team(s)/ Funding organisation(s) <sup>1</sup>	Project period	Project short name	Main Fe-clay topics	Special aspects
SKB Äspö – CT/ SKB/Posiva	2006–10	ABM	long-term corrosion, Fe profiles	in-situ study, different clay materials, first results in 1–2 years
Serco, CT, GSF, Posiva/ SKB, NF-PRO	2001–07	Anaerobic corrosion of Fe in bentonite	corrosion tests, impact on bentonite	long-term corrosion, also physical properties studied, work to continue beyond 2007
Nagra - CT/Posiva/SKB	2005–07	Fe-bentonite /KBS-3H	effects of supercontainer on bentonite perfor- mance, literature and modelling	reactive transport calculations for Olkiluoto site, study terminated
BGR	2002–10	Ideal bentonite	effect of corrosion on bentonite performance	batch tests, many bentonites tested
JAEA	1996– 2007	Long-term experiments	long-term behaviour of bentonite	experiments completed, analysis ongoing
NRI/RAWRA, NF-PRO	2004–08	var. subprojects	corrosion, diffusion of Fe, effects on bentonite	“classical” corrosion study combined with transport and alteration aspects
CEA Cadarache	2003–07	Fe-bentonite and Fe- claystone	modelling canister corro- sion effects on bentonite and claystone in French disposal concept	reactive transport calculations, study terminated
PSI/Nagra	2007–?	Fe(II) sorption	competition effects with radionuclides	batch type experiments

<sup>1</sup> A list of organisations (including abbreviations) is found in Appendix A.

## 4.2 Identified gaps and potential areas of common interest

In principle, the same uncertainties, as identified in the workshop of last year still hold.

### 4.2.1 Corrosion

The long-term anaerobic corrosion rates of steel compounds in EBS-type media are relatively well established (0.1–1  $\mu\text{m/a}$ ). The lower boundary of corrosion rates, however, is rather uncertain because the long-term behaviour of the protective film of corrosion products is not known. There is still some uncertainty on the nature of corrosion products, which depends both on thermodynamic and kinetic constraints. Especially, the kinetics of precipitation of corrosion products and their nature are not adequately known and have not been systematically studied in corrosion tests.

### 4.2.2 Smectite alteration and cementation effects

#### *Thermodynamics*

The thermodynamic relationships of clay systems, which are generally based on estimation methods, are still subject to considerable uncertainty. This is especially true for 1:1 clays, such as Fe-serpentines (e.g. berthierine). According to our knowledge, work on improved thermodynamic databases for clays is in progress by the BRGM (sponsored by Andra) and by the research team of Per Aagard at the University of Oslo.

### ***Kinetics of smectite transformation***

Kinetics is slow and this makes it difficult to produce meaningful experimental data. Moreover, contrary to illitisation, the nature of reaction products is difficult to predict. This is because of (1) large thermodynamic uncertainties, (2) poor evidence from natural low-temperature systems and (3) largely unknown reaction mechanism which involves several reaction steps. These may include de-hydroxylation or dehydration, reduction and migration of  $\text{Fe}^{2+}$  to the interlayer and to structural octahedral layer /e.g. Lantenois et al. 2005/. So far, the available experimental data on smectite-to-Fe-clay transformations has not been systematically assessed. Thus, rate constants and temperature dependence thereof are barely constrained. Currently ongoing studies may shed some light on these parameters in the near future.

It is worth noting that identification of minor clay reaction products is challenging and considerable expertise in structural and microscopic analysis is required. Besides more classical methods (e.g. XRD, XPS, SEM, Mössbauer), advanced synchrotron-based surface spectroscopy techniques (e.g.  $\mu$ -XRD,  $\mu$ -XRF) could be of great use for future studies.

### ***Cementation effects***

Cementation, as used here, refers to all precipitation processes with Fe that do not alter the smectite fraction. A typical example is Fe oxide precipitation under oxic conditions which is known to adversely affect swelling properties of swelling clays. For anoxic conditions, it is not clear what kind of cementation processes to consider and there are, to our knowledge, no good examples in natural systems for such phenomena.

### ***Effects on bulk properties (CEC, swelling pressure, hydraulic conductivity)***

It is somewhat troubling that effects induced by Fe-clay interactions on bulk properties have been very little studied. This makes it very difficult to draw conclusions for safety assessment purposes. One reason for this lack is related to the difficulty of doing reliable hydraulic measurements under strictly anoxic conditions and the standard procedures need to be adapted.

### ***Modelling***

Various reactive transport codes have been applied and have highlighted the importance of including a coupled approach to assess Fe-clay interactions under repository conditions. This has enabled to demonstrate the importance of the diffusional constraint of Fe migration. Also, the sensitivity of different variables, such as Fe concentration at the source term or dissolution and precipitation kinetics could be evaluated. On the other hand, very little work has been done on the calibration and verification of these reactive transport models. Thus, it would very useful to perform a benchmark modelling exercise with suitable datasets.

Important drawbacks of common reactive transport models also include the neglect of multi-component diffusion and diffuse double layer effects, the oversimplification of precipitation kinetics and the disregard of TM coupling. For example, the effects of precipitation on porosity are generally considered in a very crude manner, and complete clogging (and thus stop of mass transfer) often results from the models. In reality, the generation of micro-fractures at the interface between swelling and non-swelling material can be expected. Recent advances in modelling may help to overcome some of these drawbacks.



## 5 Opportunities for common research studies

Based on the outcome of the questionnaires, a number of tasks can be formulated that would help (1) to synthesize the available data and to obtain a more coherent picture on some aspects of Fe-clay interactions and (2) to reduce uncertainties in parameter and conceptual uncertainties.

### 5.1 Possible tasks

- 1) **Interpretation of available experimental corrosion and mineral alteration data.** This would include thermodynamic/kinetic modelling as well as reactive transport modelling. In specified test cases, benchmarking between the different models could be performed. Also, novel modelling approaches that, for example, include multicomponent diffusion could be applied. Also, extension of the ongoing experimental studies by extension of the analytical programme and including also e.g. analyses of changes of physical properties such as hydraulic conductivity at the end of the tests.
- 2) **Define a proposal for a common “long-term” project.** This could include on one hand diffusion experiments and on the other careful analysis of a suitable natural or archaeological analogue. In this regard, ongoing experiments in which Fe-clay interactions have already occurred for several years (e.g. FEBEX experiment at the Grimsel Test Site) could be included in the overall project. These last mentioned could also be broadened by including studies such as hydraulic conductivity at the end of the tests.
- 3) **Conduct specific hydrothermal experiments.** Reaction rates and reaction products of smectite alteration should be determined for Na- and Ca smectite under specified pH, Eh, Si activity, Na/K ratio conditions. Specific attention should be given to potential effects of the nature of the smectite (e.g. its chemical composition) on alteration.
- 4) **Develop an experimentally sound protocol.** To obtain reliable data for repository condition it is crucial to avoid oxidation by O<sub>2</sub> contamination. A challenging point in this regard is the analysis of the solid phase after reaction without affecting the sample.

### 5.2 The way ahead

From the timing of the running studies (Table 4.1) it can be seen that many are bound to end this year. This, in particular, holds for the studies performed within NF-PRO. Thus, a significant amount of new interesting data can be expected in the near future. Also, a number of individual studies (e.g. CEA, NRI/RAWRA, JAEA) will end soon. Another point is that an extensive research program on Fe-glass-clay interactions has being drafted by Andra for the next five years and will be made official shortly.

There are various possibilities how to organize future R&D on this topic for radwaste disposal purposes. These include:

- a) Business as usual: Each funding organisation formulates its own proposal with mainly its own contractors. The outcome of the studies is regularly presented at meetings. The collaboration between organisations is generally rather low, but may be enforced for specific aspects in small projects.
- b) The funding organisations create together a large common proposal: This requires a multilateral or an EC network structure. This puts a certain load on the organisational form but of course allows to create synergies and to optimise resources.

- c) A mixed organisation between a) and b): Organisations collaborate on specific topics. A good example would be the Task Force on modelling as practised within the THM modelling Task Force at Äspö. Also, one could envision a loose collaboration of the funding organisations in the form of an umbrella agreement and the organisation of regular meetings.

We suggest holding a “start-up” meeting this fall with the interested funding organisations and selected experts. In this meeting, the new results from programs, such as NF-PRO could be presented and then possibilities for collaborations and common proposals could be discussed.

## References

- Battaillon C, 2006.** Corrosion products in compacted bentonite and argillite. Fe-Bentonite Workshop, Basel (CH), 10–11 May 2006.
- Bildstein O, Trotignon L, Perronnet M, Jullien M, 2006.** Modelling iron-clay interactions in deep geological disposal conditions, *Physics and Chemistry of the Earth* 31, 10–14.
- Carlson L, Karnland O, Olsson S, Smart N, Rance A, 2006.** Experimental studies on the interaction between anaerobically corroding iron and bentonite, Posiva Working Report 2006-60. Posiva Oy, Olkiluoto, Finland.
- Carlson L, Karnland O, Oversby V M, Rance A P, Smart N R, Snellman M, Vähänen M, Werme L O, 2007.** Experimental studies of the interactions between anaerobically corroding iron and bentonite, *Physics and Chemistry of the Earth* 32, 334–345.
- Cathelineau M, Guillaume D, Mosser-Ruck R, Dubessy J, Charpentier D, Villiéras F, Michau N, 2005.** Dissolution-crystallization processes affecting dioctahedral smectite in the presence of iron: implication on mineral distribution in clay barriers, ANDRA International Conference, 14–18 March 2005, Tours, France.
- Cathelineau M, 2006.** Fe-Bentonite Workshop, Basel (CH), 10–11 May 2006.
- Charlet L, Tournassat C, 2005.** Fe(II)-Na(I)-Ca(II) cation exchange on montmorillonite in chloride medium: evidence for preferential clay adsorption of ions pairs in marine environment chemical modelling and XRD profile modelling study. *Aquatic Geochemistry* 11, 115–137.
- Charlet L, 2006.** Transfers through the reactive clay barriers in radioactive waste repositories. Surface reactions between Fe<sup>2+</sup> and smectites. in Wersin P. and Mettler S. 2006. Workshop on Fe-clay interactions in repository environments, a joint initiative by Andra, SKB and Nagra. Basel 9-10 May 2006. NAB-06-15. Nagra, Wetingen, Switzerland.
- Charlet L, et al. 2007.** Electron transfer at the mineral/water interface: Selenium reduction by ferrous iron. *Geochim. Cosmochim. Acta* (in review).
- Charpentier D, Devineau K, Mosser-Ruck R, Cathelineau M, Villiéras F, 2006.** Bentonite-iron interactions under alkaline condition: An experimental approach, *Applied Clay Science*, 32, 1–13.
- Gailhanou H, 2006.** Détermination expérimentale des propriétés thermodynamiques et étude des nanostructures de minéraux argileux, PhD thesis, Université Aix Marseille II.
- Gaucher E C, Blanc P, Bardot F, Braibant G, Buschaert S, Crouzet C, Gautier A, Girard J-P, Jacquot E, Lassin A, Negrel G, Tournassat C, Vinsot A, Altmann S, 2006.** Modelling the porewater chemistry of the Callovian-Oxfordian formation at a regional scale. *Comptes Rendus Geosciences* 338, 917–930.
- Géhin A, Grenèche J-M, Tournassat C, Brendlé J, Rancourt D G, Charlet L, 2007.** Reversible surface-sorption-induced electron-transfer oxidation of Fe(II) at reactive sites on a synthetic clay mineral, *Geochim. Cosmochim. Acta* 71 863–876
- Guillaume D, Neaman A, Cathelineau M, Mosser-Ruck R, Pfeiffert C, Abdeloula M, Dubessy J, Villiéras F, Baronnet A, Michau N, 2003.** Experimental synthesis of chlorite from smectite at 300°C in the presence of metallic Fe. *Clay Minerals* 38, 281–302.

**Guillaume D, Neaman A, Cathelineau M, Mosser-Ruck R, Pfeiffert C, Abdelmoula M, Dubessy J, Villiéras F, Michau N, 2004.** Experimental study of the transformation of smectite at 80 and 300°C in the presence of Fe oxides. *Clay Minerals* 39, 17–34.

**Karnland O, 2006.** In Wersin P. and Mettler S. 2006. Workshop on Fe-clay interactions in repository environments, a joint initiative by Andra, SKB and Nagra. Basel 9-10 May 2006. NAB-06-15. Nagra, Wettingen, Switzerland.

**Kaufhold S, Dohrmann R, 2005.** Comparative study of bentonite properties: Corrosivity and effect of drying. Poster at ANDRA International Conference, 14–18 March 2005, Tours, France.

**Lantenois S, Lanson B, Muller F, Bauer A, Jullien M, Plancon A, 2005.** Experimental study of smectite interaction with metal Fe at low temperature: 1. smectite destabilization, *Clays and Clay Minerals* 53, 597–612.

**Madsen F T, Kahr G, 1991.** Diffusion von Eisen- und Jodidionen in hochverdichtetem Bentonit, Nagra Technical Report NTB 91-28, Wettingen, Switzerland.

**Marty N, 2006.** Modélisation couplée (transport-réaction) des interactions fluides-argiles et de leurs effets en retour sur les propriétés physiques de barrières ouvragées en bentonite. PhD Thesis, University Louis Pasteur Strasbourg.

**Montes-H G, Fritz B, Clement A, Michau N, 2005a.** A simplified method to evaluate the swelling capacity evolution of a bentonite barrier related to geochemical transformations, *Applied Geochemistry* 20, 409–422.

**Montes-H G, Fritz B, Clement A, Michau N, 2005b.** Modelling of geochemical reactions and experimental cation exchange in MX80 bentonite, *Journal of Environmental Management* 77, 35–46.

**Montes-H G, Fritz B, Clement A, Michau N, 2005c.** Modeling of transport and reaction in an engineered barrier for radioactive waste confinement, *Applied Clay Science* 29, 155–171.

**Montes-H G, Marty N, Fritz B, Clement A, Michau N, 2005d.** Modelling of long-term diffusion-reaction in a bentonite barrier for radioactive waste confinement, *Applied Clay Science* 30, 181–198.

**Müller-Vonmoos M, Kahr G, Bucher F, Madsen F, Mayor P-A, 1991.** Untersuchungen zum Verhalten von Bentonit in Kontakt mit Magnetit und Eisen unter Endlagerbedingungen. Nagra Technical Report NTB 91-14. Nagra, Wettingen, Switzerland.

**Nagra, 1986.** Unpublished internal report (available upon request).

**Papillon F, Michaud V, Bataillon C, Locoge P, Jullien M, 1999.** Expériences “Module-Corrosion à 25 et 80°C” : Synthèse et analyses des résultats (Rapport Juin 1999). Commissariat à l’Energie Atomique de Saclay, Gif sur Yvette, N.T. SESD 99-35, 58 58.

**Papillon F, Jullien M, Bataillon C, 2003.** Carbon steel behaviour in compacted clay: two long term tests for corrosion prediction. In “Prediction of the long term corrosion behaviour in nuclear waste systems”. Féron and MacDonald Eds., European Federation of Corrosion Publications, 36, 439–454, Maney Publishing, UK.

**Perronet M, 2004.** Réactivité des matériaux argileux dans un contexte de corrosion métallique. Application aux stockage des déchets radioactifs en site argileux. PhD thesis Institut National Polytechnique de Lorraine, Nancy, France 288p.

**Perronet M, Villiéras F, Jullien M, Razafitianamaharavo A, Raynal J, Bonnin D, 2007.** Towards a link between the energetic heterogeneities of the edge faces of smectites and their stability in a context of metallic corrosion. *Geochim. Cosmochim. Acta* 71, 1463–1479.

- Sali D, 2003.** La modélisation du comportement physico-chimique des argiles de barrières ouvragées au contact de solutions naturelles, PhD Thesis. University Louis Pasteur Strasbourg.
- Scheinost A, Charlet, 2007.** Reduction of Fe(II) by green rust and siderite. Environ. Sci. Technol. (subm.).
- Shibata M, et al. 2002.** ANDRA International Meeting, 2002, Reims, Abstract pp.151–152, O-10b-4.
- Shibata M, et al. 2005.** “Experimental study on stability of iron (II) exchanged montmorillonite”, 13<sup>th</sup> International Clay Conference (ICC), Abstracts, p.116
- Smart N R, Rance A P, Werme L O, 2004.** Anaerobic corrosion of steel in bentonite. Mat. Res. Soc. Symp. Proc. 807, 441–446.
- Smart N R, Rance A P, Carlson L, Werme L O, 2006.** Further studies of the anaerobic corrosion of steel in bentonite. Mat. Res. Soc. Symp. Proc. 932, 813–818.
- Suyama, et al. 2006.** JAEA-Research report, 2006-064. (for 250°C) (in Japanese).
- Suyama, et al. 2007.** JAEA-Research report, 2007-018. (for 150°C) (in Japanese).
- Tournassat C, 2003.** Cations-clays interactions: the Fe(II) case. Application to the problematic of the French deep nuclear repository field concept. PhD thesis, University of Grenoble, France, 199 p.
- Tournassat C, Charlet L, Favre F, Greneche J P, 2007.** Interactions of metals and H<sub>4</sub>SiO<sub>4</sub> at clay/water interface. Part I. Fe(II) high affinity for natural montmorillonite and implications in anoxic and iron-rich systems modelling. Geochim. Cosmochim. Acta (in review).
- Vejsada J, 2006.** The uncertainties associated with the application of batch technique for distribution coefficients determination – a case study of cesium adsorption on four different bentonites, Applied Radiation and Isotopes, 64, 1538–1548.
- Vejsada J, Vopálka D, Filipská H, Vokál A, 2006.** Study of caesium sorption on Na and Ca-Mg bentonites using batch and diffusion experiments, Czechoslovak Journal of Physics, 56, Suppl. D, D73-D80.
- Vokál A, et al. 2006a.** Research of effect of corrosion products on carbon steel corrosion in bentonite environment, 3<sup>rd</sup> General Meeting and Workshop of NF-PRO Project, El Escorial, Spain, 14–16. November 2006.
- Vokál A, Lukin D, Vopálka D, 2006b.** Carbon Steel Canister Performance Assessment: Iron Transfer Study, Materials Research Society Symp. Proc. 932, 877–882.
- Wersin P, Johnson L H, Snellman M, 2005.** Impact of iron released from steel components on the performance of the bentonite buffer: a preliminary assessment within the framework of the KBS-3H disposal concept. Mat. Soc. Res. Symp. Proc. 932, Ghent.
- Wersin P, Mettler S, 2006 (eds.).** Workshop on Fe-clay interactions in repository environments, a joint initiative by Andra, SKB and Nagra. Basel / Switzerland, 9–10 May 2006. Nagra Arbeitsbericht NAB 06-15.
- Wersin P, Birgersson M, Olsson S, Karnland O, Snellman M, 2007.** Impact of corrosion-derived iron on the bentonite buffer within the KBS-3H disposal concept. The Olkiluoto site as case study. POSIVA 2007-11 and SKB R-08-34. Posiva Oy, Olkiluoto, Finland and Swedish Nuclear Fuel and Waste Management Co (SKB), Stockholm, Sweden.
- Wilson J, Cressey G, Cressey B, Cuadros J, Ragnarsdottir K V, Savage D, Shibata M, 2006a.** The effect of iron on montmorillonite stability: (II) Experimental investigation. Geochim. Cosmochim. Acta 70, 323–336.

**Wilson J, Savage D, Cuadros J, Shibata M, Ragnarsdottir K V, 2006b.** The effect of iron on montmorillonite stability. (I) Background and thermodynamic considerations. *Geochim. Cosmochim. Acta* 70, 306–322.

### List of organisations

Abbreviation	Name	Country
Andra	Agence nationale	France
BGR	Bundesanstalt für Geowissenschaften und Rohstoffe	Germany
BRGM	Bureau de recherches géologiques et minières	France
CEA	Commissariat d'Énergie Atomique	France
CGS	Centre de Géochimie de Surface at University Louis Pasteur	France
CT	Clay Technology Ltd.	Sweden
ETH	Federal Institute of Technology	Switzerland
GSF	Geological Survey of Finland	Finland
JAEA	Japan Atomic Energy Agency	Japan
Nagra	National Cooperative for the Disposal of Radioactive Waste	Switzerland
NRI	Nuclear Research Institute	Czech Republic
Numo	Nuclear Waste Organisation of Japan	Japan
Posiva	Posiva Oy	Finland
PSI	Paul Scherrer Institute	Switzerland
Quintessa	Quintessa Ltd.	United Kingdom
Serco	Serco Assurance	United Kingdom
SKB	Swedish Nuclear Fuel and Waste Management Co	Sweden
Uni Bern	University of Bern	Switzerland
Uni Bristol	University of Bristol	United Kingdom
Uni Grenoble	University of Grenoble	France
Uni Nancy	University of Nancy	France

## Listing of questionnaires

### Iron-bentonite/smectite interactions – ongoing or planned study

Date: 11/01/07

Authors: Paul Wersin

Responsible organisation: Posiva, SKB

Study – Basic information	Materials used	Experimental conditions	Results/Analyses	Documentation
1. Title of study. 2. Main investigator/organisation and e-mail. 3. Associates labs, funding organisation. 4. Timing of study (start/end). 5. Main objectives. 6. Status of work (Jan 07). 7. Planned work. 8. Info on modelling (approach, codes). 9. Other important info.	1. Type of bentonite/smectite. 2. Sample density (powder, compacted). 3. Iron compound added (e.g Fe, Fe <sub>3</sub> O <sub>4</sub> , Fe(II) solution....). 4. Type of iron compound (wire, coupon...). 5. Background electrolyte, other chemicals added.	1. Solid/liquid ratio. 2. Clay/Fe ratio. 3. Size of samples, volumes. 4. Temperature. 5. pH. 6. Redox conditions (N <sub>2</sub> , Ar ....). 7. Type of experiments (batch, column, natural analogues....). 8. Duration of test.	1. Analytical methods (solid, solution). 2. Corrosion results (rates, corrosion products, gas production ....). 3. Mineralogical results (reaction products, iron species, cementing effects ....). 4. Solution results (pH, solutes). 5. Physico-chemical properties (swelling pressure, CEC...). 6. Conclusions from data/modelling.	1. Unpublished reports. 2. Published reports. 3. Papers.
1. Impact of corrosion-derived iron on the bentonite buffer within the KBS-3H disposal concept. The Olkiluoto site as case study.	1. MX-80.	Not applicable (no experiments performed).	6. From mass balance: maximum of 30% of swelling clay affected; from reactive transport calculations: only small spatial area around iron source affected because of coupled mass transfer and geochemical constraints.	2. /Johnson et al. 2005/ Posiva Working Report 2005-09. /Wersin et al. 2007/ Posiva Report (in prep.)
2. Paul Wersin, Nagra, paul.wersin@nagra.ch.	2. Dry density: 1.6 Mg/m <sup>3</sup> .			3. /Wersin et al. 2005/, Mat. Res. Soc. Symp. Proc. 932, 95-102.
3. Clay Technology, Posiva/SKB.	3. Iron from supercontainer.			
4. 2005–2007.				



<b>Study – Basic information</b>	<b>Materials used</b>	<b>Experimental conditions</b>	<b>Results/Analyses</b>	<b>Documentation</b>
5. Determine safety-relevant effects from Fe-bentonite interactions, assess impact of Fe on buffer's stability, recommend further work.				
6. Draft report on study available.				
7. Not decided yet.				
8. Mass balance calculations, reactive transport modelling with Phreeqc and Crunchflow.				
9. Literature review and modelling study (no experiments).				

## Iron-bentonite/smectite interactions – ongoing or planned study

Date: 15/01/07

Authors: **Margit Snellman**

Responsible organisation: **Posiva, SKB**

Study – Basic information	Materials used	Experimental conditions	Results/Analyses	Documentation
<ol style="list-style-type: none"> <li>Title of study.</li> <li>Main investigator/organisation and e-mail.</li> <li>Associates labs, funding organisation.</li> <li>Timing of study (start/end).</li> <li>Main objectives.</li> <li>Status of work (Jan 07).</li> <li>Planned work.</li> <li>Info on modelling (approach, codes).</li> <li>Other important info.</li> </ol>	<ol style="list-style-type: none"> <li>Type of bentonite/smectite.</li> <li>Sample density (powder, compacted).</li> <li>Iron compound added (e.g Fe, Fe<sub>3</sub>O<sub>4</sub>, Fe(II) solution....).</li> <li>Type of iron compound (wire, coupon...).</li> <li>Background electrolyte, other chemicals added.</li> </ol>	<ol style="list-style-type: none"> <li>Solid/liquid ratio.</li> <li>Clay/Fe ratio.</li> <li>Size of samples, volumes.</li> <li>Temperature.</li> <li>pH.</li> <li>Redox conditions (N<sub>2</sub>, Ar ....).</li> <li>Type of experiments (batch, column, natural analogues....).</li> <li>Duration of test.</li> </ol>	<ol style="list-style-type: none"> <li>Analytical methods (solid, solution).</li> <li>Corrosion results (rates, corrosion products, gas production ....).</li> <li>Mineralogical results (reaction products, iron species, cementing effects ....).</li> <li>Solution results (pH, solutes).</li> <li>Physico-chemical properties (swelling pressure, CEC...).</li> <li>Conclusions from data/modelling.</li> </ol>	<ol style="list-style-type: none"> <li>Unpublished reports.</li> <li>Published reports.</li> <li>Papers.</li> </ol>
<ol style="list-style-type: none"> <li>Impact of iron on bentonite within the KBS-3H concept. Experimental studies on the interaction between anaerobically corroding iron and bentonite.</li> </ol>	<ol style="list-style-type: none"> <li>MX-80.</li> </ol>	<ol style="list-style-type: none"> <li>Test cells with compacted bentonite in contact with an outer electrolyte solution (S/L not reported).</li> </ol>	<ol style="list-style-type: none"> <li>Analysis of solid only. SEM-EDX and EMPA, laser Raman spectroscopy, anoxic XRD and Mössbauer spectroscopy, oxic XRD, FTIR, TEM-EDS, CEC and exchangeable cations and total chemical composition.</li> </ol>	<ol style="list-style-type: none"> <li>/Carlson et al. 2006/, Posiva Working Report 2006-60.</li> </ol>
<ol style="list-style-type: none"> <li>Liisa Carlson, GSF. Nick Smart, Sercoassurance. Nick.smart@sercoassurance.com</li> <li>Clay Technology, Posiva/SKB.</li> </ol>	<ol style="list-style-type: none"> <li>Saturated bulk density.</li> <li>Mg/m<sup>3</sup>.</li> <li>Fe and Carbon steel (0,21% C).</li> </ol>	<ol style="list-style-type: none"> <li>a) Coupon tests 82,6 g clay/5.5 g iron.</li> <li>b) Wire tests 64.6 g clay/75 g iron.</li> <li>Test cell volume 42 cm<sup>3</sup>. a) Coupon tests: clay 82,6 g, coupons 5,5 g, a total surface area of coupons 0.0009 m<sup>2</sup>. b) Wire tests: clay 64,6 g, wires 75 g, total surface area of wires 0.1 m<sup>2</sup>.</li> </ol>	<ol style="list-style-type: none"> <li>Corrosion rates not reported in this study. Corrosion products identified were hematite, goethite and magnetite.</li> <li>a) Coupon tests: No major changes in the bentonite. A narrow zone of corrosion products in the bentonite (0.15–1.25 mm thick). b) Wire tests: bentonite strongly aggregated and had a brackish or bluish green colour character typical for reducing conditions.</li> </ol>	<ol style="list-style-type: none"> <li>/Carlson et al. 2006/, J. Physics and Chemistry of the Earth (in press). /Smart et al. 2005/, MRS 2005.</li> </ol>

Study – Basic information	Materials used	Experimental conditions	Results/Analyses	Documentation
			<p>The proportion of iron in the Fe<sup>2+</sup> oxidation state increased from 36% in fresh bentonite to 74–78%. Some of the Fe<sup>3+</sup> in the octahedral montmorillonite sheets may have been reduced to Fe<sup>2+</sup>. Iron entered into the bentonite matrix, up to 20% near corroding wires. Iron content of bentonite matrix increased more than needed to saturate the exchange sites of MX-80.</p> <p>No Fe-rich clay minerals were formed. No iron oxyhydroxide minerals such as magnetite or Fe(OH)<sub>2</sub> could be identified with the methods used.</p>	
4. 2004–2006.	<p>4. a) Cast iron (1 mm thick) and carbon steel coupons (3 mm thick).</p> <p>b) Carbon steel wires, 5 mm length and 0.4 mm diameter.</p>	4. 30°C and 50°C.	4. No analyses of solutions.	
5. To investigate how mineralogical, chemical and technical characteristics of bentonite are changed by contact with iron.	5. 31.6 g/L NaCl + 1.1 g/L Na <sub>2</sub> CO <sub>3</sub> solution at a pH of 10.4.	5. pH of electrolyte solution contacted with bentonite was 10.4.	<p>5. A significant increase in hydraulic conductivity for wire tests at 50°C. Incorporation of iron resulted in a loss of CEC, suggesting adsorption possibly onto favoured sites of sheet surfaces or mineral discontinuities in the montmorillonite.</p> <p>No change in swelling pressure was observed.</p>	
6. Work completed.		6. Samples were prepared and sealed in nitrogen atmosphere and tests were performed in gas cells.	6. In the tests with carbon steel wires, an incorporation of iron into the bentonite at concentration levels	

Study – Basic information	Materials used	Experimental conditions	Results/Analyses	Documentation
			<p>of 7–8% resulted in lower CEC and a higher hydraulic conductivity. The increase in iron of the bentonite has probably several explanations, including surface adsorption of some Na<sup>+</sup> in the interlayer positions of montmorillonite by non-exchangeable Fe(II) complexes. There may also have been some very unstable oxidised iron compounds present that were not identified. The hydraulic conductivity increase may partly be explained by the exchange reactions, but may also be due to inhomogeneities, local density differences eventually due to presence of iron-rich particles or cementing iron compounds in the matrix.</p>	
<p>7. Serco/SKB planning continuation of tests with corrosion of iron in bentonite.</p>		<p>7. Batch experiments (test cells with iron wires or coupons added to compacted bentonite).</p>		
<p>8. No modelling performed.</p>		<p>8. Coupon tests: 356 days at 50oC and 900 days at 30oC.  Wire tests: 829 days at 30oC and 911 days at 50oC.</p>		
<p>9. 1. Alternative buffer material experiment. 2. SKB Project. Project leader is Anders Eng, Acuo. Subproject leader and responsible for analysis program is Daniel Svensson, SKB (daniel.svensson@skb.se).</p>	<p>1. MX80, Friedland, Dep CA-N, Ibeco-Seal M-90, Asha 505, Callovo Oxfordian (argillite claystone), Rokle, Febex, Ikosorb, Calcigel, Japanese Na bentonite (kunigel?). 2. Compacted blocks. 3. Fe.</p>	<p>1. Buffer density. 2. Surface limited. 3. Approximately 10 kg per clay block. 4. Ca 130°C. 5. Uncontrolled, determined mainly by the different clays. 6. Uncontrolled, probably reducing, at least in the longer experiments.</p>	<p>Test program is being developed. Due to the large amount of different materials, one cannot go into to many details. The goal is to track fundamental chemical and mineralogical changes and if possible their effect on the physical properties. Daniel Svensson is</p>	

Study – Basic information	Materials used	Experimental conditions	Results/Analyses	Documentation
<p>3. Several international participating organisations.</p> <p>4. 2006–2011.</p> <p>5. Three heated iron-canisters are used with 13 different buffer materials in “LOT scale”. The first package will be taken up after one year and the first report is expected to be finished in 2009.</p> <p>6. Packages are installed and heaters activated. Lab test program for the materials is being developed.</p> <p>7. Analysis of reference materials and exposed material mainly regarding chemistry and mineralogical properties.</p> <p>8. No modelling is planned.</p>	<p>4. Iron canister.</p> <p>5. Äspö groundwater.</p>	<p>7. “Largescale” canister type experiment at Äspö Hardrock Laboratory.</p> <p>8. 1–5 years for different packages.</p>	<p>planning to study some of the parts in more detail as a part in his Ph.D. research.</p>	

## Iron-bentonite/smectite interactions – ongoing or planned study

Date: 17/01/07

Authors of this questionnaire: **Stephan Kaufhold**

Responsible organisation: **BGR**

Study – Basic information	Materials used	Experimental conditions	Results/Analyses	Documentation
<ol style="list-style-type: none"> <li>Title of study.</li> <li>Main investigator /organisation and e-mail.</li> <li>Associates labs, funding organisation.</li> <li>Timing of study (start/end).</li> <li>Main objectives.</li> <li>Status of work (Jan 07).</li> <li>Planned work.</li> <li>Info on modelling (approach, codes).</li> <li>Other important info.</li> </ol>	<ol style="list-style-type: none"> <li>Type of bentonite/smectite.</li> <li>Sample density (powder, compacted).</li> <li>Iron compound added (e.g Fe, Fe<sub>3</sub>O<sub>4</sub>, Fe(II) solution....).</li> <li>Type of iron compound (wire, coupon...).</li> <li>Background electrolyte, other chemicals added.</li> </ol>	<ol style="list-style-type: none"> <li>Solid/liquid ratio.</li> <li>Clay/Fe ratio.</li> <li>Size of samples, volumes.</li> <li>Temperature.</li> <li>pH.</li> <li>Redox conditions (N<sub>2</sub>, Ar ....).</li> <li>Type of experiments (batch, column, natural analogues....).</li> <li>Duration of test.</li> </ol>	<ol style="list-style-type: none"> <li>Analytical methods (solid, solution).</li> <li>Corrosion results (rates, corrosion products, gas production ....).</li> <li>Mineralogical results (reaction products, iron species, cementing effects ....).</li> <li>Solution results (pH, solutes).</li> <li>Physico-chemical properties (swelling pressure, CEC...).</li> <li>Conclusions from data/modelling.</li> </ol>	<ol style="list-style-type: none"> <li>Unpublished reports.</li> <li>Published reports.</li> <li>Papers.</li> </ol>
<ol style="list-style-type: none"> <li>"Ideal bentonite" (here: with respect to corrosivity).</li> </ol>	<ol style="list-style-type: none"> <li>Forty different materials, mainly bentonites, large deposits from all over the world.</li> </ol>	<ol style="list-style-type: none"> <li>S/L ratio depended on consistency of gel (between 50 and 100% water, ref. to dry mass).</li> </ol>	<ol style="list-style-type: none"> <li>Gravimetric.</li> </ol>	<p>/Kaufhold and Dohrmann 2005/: Comparative study of bentonite properties: Corrosivity and effect of drying. – Poster at Andra meeting, Tours, 2005.</p>
<ol style="list-style-type: none"> <li>Stephan Kaufhold, Reiner Dohrmann, s.kaufhold@bgr.de, r.dohrmann@bgr.de</li> </ol>	<ol style="list-style-type: none"> <li>Powder, gel.</li> </ol>	<ol style="list-style-type: none"> <li>Undefined, consistency of the gel was kept similar.</li> </ol>	<ol style="list-style-type: none"> <li>Degree of mass loss of wire.</li> </ol>	
<ol style="list-style-type: none"> <li>BGR, Hannover.</li> </ol>	<ol style="list-style-type: none"> <li>Iron (Fe<sup>0</sup>).</li> </ol>	<ol style="list-style-type: none"> <li>10 g gel with ca. 1 g wire.</li> </ol>	<p>–</p>	
<ol style="list-style-type: none"> <li>2002–2010.</li> </ol>	<ol style="list-style-type: none"> <li>Wire.</li> </ol>	<ol style="list-style-type: none"> <li>Room.</li> </ol>	<p>–</p>	
<ol style="list-style-type: none"> <li>Identification of the optimum bentonite for HLRW repositories.</li> </ol>	<ol style="list-style-type: none"> <li>Deionized water as well as 5% NaCl solution.</li> </ol>	<ol style="list-style-type: none"> <li>Depending on bentonite type, not stabilised.</li> </ol>	<p>–</p>	
<ol style="list-style-type: none"> <li>First comparative tests were performed, further work required is currently planned.</li> </ol>		<ol style="list-style-type: none"> <li>Ambient conditions.</li> </ol>	<ol style="list-style-type: none"> <li>Corrosive bentonites could be distinguished from less corrosive ones, correlation of corrosivity with material properties (pH, Cl content,..) failed.</li> </ol>	

Study – Basic information	Materials used	Experimental conditions	Results/Analyses	Documentation
7. Bentonite FeCl <sub>2</sub> solution interaction in long term tests.		7. Closed glass vessel.		
8. No modelling performed.		8. 1 month.		

## Iron-bentonite/smectite interactions – ongoing or planned study

Date: 5/03/07

Authors: **Olivier Bildstein**

Responsible organisation: **CEA**

Study – Basic information	Materials used	Experimental conditions	Results/Analyses	Documentation
<ol style="list-style-type: none"> <li>Title of study.</li> <li>Main investigator /organisation and e-mail.</li> <li>Associates labs, funding organisation.</li> <li>Timing of study (start/end).</li> <li>Main objectives.</li> <li>Status of work (Jan 07).</li> <li>Planned work.</li> <li>Info on modelling (approach, codes).</li> <li>Other important info.</li> </ol>	<ol style="list-style-type: none"> <li>Type of bentonite/smectite.</li> <li>Sample density (powder, compacted).</li> <li>Iron compound added (e.g Fe, Fe<sub>3</sub>O<sub>4</sub>, Fe(II) solution....).</li> <li>Type of iron compound (wire, coupon...).</li> <li>Background electrolyte, other chemicals added.</li> </ol>	<ol style="list-style-type: none"> <li>Solid/liquid ratio.</li> <li>Clay/Fe ratio.</li> <li>Size of samples, volumes.</li> <li>Temperature.</li> <li>pH.</li> <li>Redox conditions (N<sub>2</sub>, Ar ....).</li> <li>Type of experiments (batch, column, natural analogues....).</li> <li>Duration of test.</li> </ol>	<ol style="list-style-type: none"> <li>Analytical methods (solid, solution).</li> <li>Corrosion results (rates, corrosion products, gas production ....).</li> <li>Mineralogical results (reaction products, iron species, cementing effects ....).</li> <li>Solution results (pH, solutes).</li> <li>Physico-chemical properties (swelling pressure, CEC...).</li> <li>Conclusions from data/modelling.</li> </ol>	<ol style="list-style-type: none"> <li>Unpublished reports.</li> <li>Published reports.</li> <li>Papers.</li> </ol>
<ol style="list-style-type: none"> <li>Experimental study of the iron-bentonite interactions in repository conditions.</li> </ol>	<ol style="list-style-type: none"> <li>Mainly FoCa7 (some experiments with MX-80, Prassa, I/S FzGr1, Tournemire claystone).</li> </ol>	<ol style="list-style-type: none"> <li>Batch cells with a mixtures of different proportions of bentonite and iron powder, Evian water with S/L ratio of 1/16.7.</li> </ol>	<ol style="list-style-type: none"> <li>Analysis of solid : SEM-EDX, XRD, Mössbauer, FTIR, TEM-EDS, CEC. Solution analysis at 25°C : Eh, pH, major cations.</li> </ol>	<ol style="list-style-type: none"> <li>/Perronnet 2005/, PhD Thesis.</li> </ol>
<ol style="list-style-type: none"> <li>Michel Jullien, CEA. michel.jullien@cea.fr p/o Murielle Perronnet (present address: NASA, Houston).</li> <li>CEA.</li> </ol>	<ol style="list-style-type: none"> <li>Clay and iron powder.</li> </ol>	<ol style="list-style-type: none"> <li>Different C/F were tested: 1/30, 1/15, 1/7.5, 1/5, 1/3.75, 1/3 (some materials at 1/1).</li> <li>Batch cell volume: 100 cm<sup>3</sup>.</li> </ol>	<ol style="list-style-type: none"> <li>Corrosion rates not reported in this study. Main corrosion products identified were Fe-rich serpentine.</li> <li>Initial smectites dissolution.</li> </ol>	<ol style="list-style-type: none"> <li>/Perronnet et al. 2007/, Clay and Clay minerals.</li> </ol>
<ol style="list-style-type: none"> <li>2001–2004.</li> </ol>		<ol style="list-style-type: none"> <li>25°C, 80°C, and 150°C.</li> </ol>	<ol style="list-style-type: none"> <li>pH of electrolyte solution contacted with bentonite was up to 9.4 at the end of the experiments (maximum for a C/F ratio of 1/3).</li> </ol>	
<ol style="list-style-type: none"> <li>To investigate how mineralogical composition, chemistry and retention (CEC) properties of bentonite are changed by contact with iron.</li> </ol>	<ol style="list-style-type: none"> <li>Evian water (a CO<sub>3</sub>-Ca-Mg water). CO<sub>3</sub> = 357 mg/L Ca = 78 mg/L Mg = 24 mg/L</li> </ol>	<ol style="list-style-type: none"> <li>Initial pH 7.4 (25°C).</li> </ol>	<ol style="list-style-type: none"> <li>Incorporation of iron resulted in a loss of CEC.</li> </ol>	



Study – Basic information	Materials used	Experimental conditions	Results/Analyses	Documentation
6. Work completed.		6. Anoxic conditions (hand-box in nitrogen atmosphere) were imposed only for the retrieval of solutions).	6. There is a F/C threshold (1/7.5) above which Ferich 7A serpentine type minerals become the major corrosion product as a result of the alteration of the initial smectites. The consequences are a loss exchange and swelling capacity of the bentonite.	
7.		7. Batch experiments (test cells with iron/clay mixture).		
8. No modelling performed.		8. 1, 3, 6 and 12 months.		

## Iron-bentonite/smectite interactions – ongoing or planned study

Date: 5/03/07

Authors: **Olivier Bildstein**

Responsible organisation: **CEA**

Study – Basic information	Materials used	Experimental conditions	Results/Analyses	Documentation
<ol style="list-style-type: none"> <li>Title of study.</li> <li>Main investigator/ organisation and e-mail.</li> <li>Associates labs, funding organisation.</li> <li>Timing of study (start/end).</li> <li>Main objectives.</li> <li>Status of work (Jan 07).</li> <li>Planned work.</li> <li>Info on modelling (approach, codes).</li> <li>Other important info.</li> </ol>	<ol style="list-style-type: none"> <li>Type of bentonite/smectite.</li> <li>Sample density (powder, compacted).</li> <li>Iron compound added (e.g Fe, Fe<sub>3</sub>O<sub>4</sub>, Fe(II) solution....).</li> <li>Type of iron compound (wire, coupon...).</li> <li>Background electrolyte, other chemicals added.</li> </ol>	<ol style="list-style-type: none"> <li>Solid/liquid ratio.</li> <li>Clay/Fe ratio.</li> <li>Size of samples, volumes.</li> <li>Temperature.</li> <li>pH.</li> <li>Redox conditions (N<sub>2</sub>, Ar ....).</li> <li>type of experiments (batch, column, natural analogues....).</li> <li>Duration of test.</li> </ol>	<ol style="list-style-type: none"> <li>Analytical methods (solid, solution).</li> <li>Corrosion results (rates, corrosion products, gas production ....).</li> <li>Mineralogical results (reaction products, iron species, cementing effects ....).</li> <li>Solution results (pH, solutes).</li> <li>Physico-chemical properties (swelling pressure, CEC...).</li> <li>Conclusions from data/modelling.</li> </ol>	<ol style="list-style-type: none"> <li>Unpublished reports.</li> <li>Published reports.</li> <li>Papers.</li> </ol>
<ol style="list-style-type: none"> <li>Experimental study of the iron-bentonite interactions in repository conditions.</li> </ol>	<ol style="list-style-type: none"> <li>FoCa7.</li> </ol>	<ol style="list-style-type: none"> <li>Percolation cells (hydrostatic pressure = 30 bar, flow rate = 1 ml/day).</li> </ol>	<ol style="list-style-type: none"> <li>Analysis of solid : SEM-EDX, XRD, Mössbauer, FTIR, TEM-EDS, solution analysis at 25°C : Eh, pH, major cations.</li> </ol>	<ol style="list-style-type: none"> <li>/Papillon et al. 1999/ Expériences. "Module-Corrosion à 25 et 80°C": Synthèse et analyses des résultats (Rapport Juin 1999). Commissariat à l'Energie Atomique de Saclay, Gif sur Yvette, N.T. SESD 99-35, 58 58.</li> </ol>
<ol style="list-style-type: none"> <li>Michel Jullien, CEA michel.jullien@cea.fr p/o Francine Papillon (present address: U. Pittsburgh, USA).</li> <li>CEA.</li> </ol>	<ol style="list-style-type: none"> <li>Compacted clay (1.35 g/cm<sup>3</sup>).</li> </ol>	<ol style="list-style-type: none"> <li>5 steel coupons in a cell.</li> <li>Percolation cell volume: 100 cm<sup>3</sup>.</li> </ol>	<ol style="list-style-type: none"> <li>Corrosion rates = 4 m/an at 25°C (generalized corrosion). 5.3 mm/8 months at 80°C (Averaged value because of heterogeneous pitting corrosion). Main corrosion product identified was magnetite, (+ berthierine and greenish aspect of clay at interface siderite + green rust + bacterial activity?). Production of H<sub>2</sub> gas.</li> </ol>	<ol style="list-style-type: none"> <li>/Papillon 2003/ Carbon steel behaviour in compacted clay: two long term tests for corrosion prediction. In "Prediction of the long term corrosion behaviour in nuclear waste systems". Féron and MacDonald Eds., European Federation of Corrosion Publications, 36, 439-454, Maney Publishing, UK.</li> </ol>

Study – Basic information	Materials used	Experimental conditions	Results/Analyses	Documentation
			3. Precipitation of calcite at the iron-clay interface.	
4. 1997–2000.	3. Low-alloy steel (XC38).	4. 25°C and 80°C.	4. Initial smectite is altered.	
5. To investigate iron coupons corrosion in clay.	4. Steel coupons (50x20x2 mm).	5. initial pH 7.9 (25°C).	5.	
6. Work completed.	5. In situ granitic water (Bernadan, France) sampled at –645 m (preserving gases and redox).	6. Eh = –220 mV (anoxic conditions).	6. Different mode of corrosion: generalized corrosion at 25°C, pitting corrosion at 80°C.  Initial smectites is altered. Quartz is also altered.  Newly formed Fe-Al-silicates may form from remaining bricks of the altered smectite.	
7.		7. Percolation experiments (flow rate = 1 ml/day).		
8. No modelling performed.		8. 6 months at 25°C, 8 months at 80°C.		

## Iron-bentonite/smectite interactions – ongoing or planned study

Date: 07/03/07

Authors: **Olivier Bildstein, Laurent Trotignon**

Responsible organisation: **CEA**

Study – Basic information	Materials used	Experimental conditions	Results/Analyses	Documentation
<ol style="list-style-type: none"> <li>1. Title of study.</li> <li>2. Main investigator/ organisation and e-mail.</li> <li>3. Associates labs, funding organisation.</li> <li>4. Timing of study (start/end).</li> <li>5. Main objectives.</li> <li>6. Status of work (Jan 07).</li> <li>7. Planned work.</li> <li>8. Info on modelling (approach, codes).</li> <li>9. Other important info.</li> </ol>	<ol style="list-style-type: none"> <li>1. Type of bentonite/ smectite.</li> <li>2. Sample density (powder, compacted).</li> <li>3. Iron compound added (e.g Fe, Fe<sub>3</sub>O<sub>4</sub>, Fe(II) solution....).</li> <li>4. Type of iron compound (wire, coupon...).</li> <li>5. Background electrolyte, other chemicals added.</li> </ol>	<ol style="list-style-type: none"> <li>1. Solid/liquid ratio.</li> <li>2. Clay/Fe ratio.</li> <li>3. Size of samples, volumes.</li> <li>4. Temperature.</li> <li>5. pH.</li> <li>6. Redox conditions (N<sub>2</sub>, Ar ....).</li> <li>7. Type of experiments (batch, column, natural analogues....).</li> <li>8. Duration of test.</li> </ol>	<ol style="list-style-type: none"> <li>1. Analytical methods (solid, solution).</li> <li>2. Corrosion results (rates, corrosion products, gas production ....).</li> <li>3. Mineralogical results (reaction products, iron species, cementing effects ....).</li> <li>4. Solution results (pH, solutes).</li> <li>6. Physico-chemical properties (swelling pressure, CEC...).</li> <li>7. Conclusions from data/modelling.</li> </ol>	<ol style="list-style-type: none"> <li>1. Unpublished reports.</li> <li>2. Published reports.</li> <li>3. Papers.</li> </ol>
<ol style="list-style-type: none"> <li>1. Impact of corrosion-derived iron on the bentonite buffer within the Andra disposal concept for HLW. Comparison between bentonite and claystone behaviour. The Bure site as case study.</li> </ol>	<ol style="list-style-type: none"> <li>1. MX-80 and/or Bure claystone.</li> </ol>	<p>Not applicable (no experiments performed).</p>	<ol style="list-style-type: none"> <li>2. Corrosion products = <ul style="list-style-type: none"> <li>- with Bure claystone: mainly magnetite 80%, some Fe-silicate 15% (croenstidite), also some Fe-Al-Si (Chamosite) a few %.</li> <li>- with bentonite: same proportion of magnetite and cronstedtite, a few % chamosite.</li> </ul> </li> </ol>	<ol style="list-style-type: none"> <li>2. /Bildstein 2006/, NFPro report D5.1.12.</li> </ol>
<ol style="list-style-type: none"> <li>2. Olivier Bildstein, olivier.bildstein@cea.fr.</li> </ol>	<ol style="list-style-type: none"> <li>2. Compacted, porosity = 30%.</li> </ol>		<ol style="list-style-type: none"> <li>3. Porosity decrease and clogging is expected in a few centimetre around the canister; primary smectite dissolution and precipitation of 7A Fe and Fe-Al silicates in few centimetres around canister (+6% in bentonite, +15% in claystone).</li> </ol>	<ol style="list-style-type: none"> <li>3. /Bildstein et al. 2006/, J. Chem. Phys. Earth.</li> </ol>
<ol style="list-style-type: none"> <li>3. CEA.</li> </ol>	<ol style="list-style-type: none"> <li>3. Iron from container corrosion.</li> </ol>		<ol style="list-style-type: none"> <li>4. pH rises to 10 at the iron-clay interface.</li> </ol>	

Study – Basic information	Materials used	Experimental conditions	Results/Analyses	Documentation
4. 2003–2007.	4. Container is represented as a porous media.		6. From reactive transport calculations in purely diffusive porous media: clogging is expected in the surface of the canister (extent : a few centimetres); primary smectite dissolution and precipitation of 7A Fe and Fe-Al silicates in few centimetres around canister accompanied by some porosity enhancement.	
5. Determine effect of iron-clay interactions on clay properties (CEC, swelling).				
6. Finished.				
7. Focusing on understanding porosity clogging, sensitivity calculations to determine secondary minerals as a function of pCO <sub>2</sub> , pH <sub>2</sub> , corrosion rate.				
8. Reactive transport modelling with Hytec and Crunchflow.				
9. Literature review + parameters from experiments made at lab (identifying secondary minerals, corrosion rate) and modelling study.				

## Iron-bentonite/smectite interactions – ongoing or planned study

Date: 31/01/07

Authors of this questionnaire: **Kenichi Ueno**

Responsible organisation: **JAEA**

Study – Basic information	Materials used	Experimental conditions	Results/Analyses	Documentation
<ol style="list-style-type: none"> <li>Title of study.</li> <li>Main investigator /organisation and e-mail.</li> <li>Associates labs, funding organisation.</li> <li>Timing of study (start/end).</li> <li>Main objectives.</li> <li>Status of work (Jan 07).</li> <li>Planned work.</li> <li>Info on modelling (approach, codes).</li> <li>Other important info.</li> </ol>	<ol style="list-style-type: none"> <li>Type of bentonite/smectite.</li> <li>Sample density (powder, compacted).</li> <li>Iron compound added (e.g Fe, Fe<sub>3</sub>O<sub>4</sub>, Fe(II) solution....).</li> <li>Type of iron compound (wire, coupon...).</li> <li>Background electrolyte, other chemicals added.</li> </ol>	<ol style="list-style-type: none"> <li>Solid/liquid ratio.</li> <li>Clay/Fe ratio.</li> <li>Size of samples, volumes.</li> <li>Temperature.</li> <li>pH.</li> <li>Redox conditions (N<sub>2</sub>, Ar ....).</li> <li>Type of experiments (batch, column, natural analogues....).</li> <li>Duration of test.</li> </ol>	<ol style="list-style-type: none"> <li>Analytical methods (solid, solution).</li> <li>Corrosion results (rates, corrosion products, gas production ....).</li> <li>Mineralogical results (reaction products, iron species, cementing effects ....).</li> <li>Solution results (pH, solutes).</li> <li>Physico-chemical properties (swelling pressure, CEC...).</li> <li>Conclusions from data/modelling.</li> </ol>	<ol style="list-style-type: none"> <li>Unpublished reports.</li> <li>Published reports.</li> <li>Papers.</li> </ol>
<ol style="list-style-type: none"> <li>Title of study. Long-term (4 years) experiments for bentonite-iron interaction.</li> </ol>	<ol style="list-style-type: none"> <li>Type of bentonite/smectite. Kunigel V1.</li> </ol>	<ol style="list-style-type: none"> <li>Size of samples, volumes. Fe-coupon: 30x30x2 mm. Bentonite: 42 (diameter) x14 mm.</li> </ol>	<ol style="list-style-type: none"> <li>Analytical methods (solid, solution). Solid analysis. XRD, SEM/EDS, TEM/EDS.</li> </ol>	Papers. /Shibata et al. 2002/ ANDRA International Meeting, 2002, Reims, abstract pp.151–152, O-10b-4.
<ol style="list-style-type: none"> <li>Main investigator /organisation and e-mail. Masahiro SHIBATA, JAEA Hiroshi SASAMOTO, JAEA Kenichi UENO, JAEA ueno.kenichi@jaea.go.jp</li> </ol>	<ol style="list-style-type: none"> <li>Sample density (powder, compacted). Compacted. Kunigel V1 (dry density:1.8 g/cm<sup>3</sup>).</li> </ol>	<ol style="list-style-type: none"> <li>Temperature. 80 (°C).</li> </ol>	<ol style="list-style-type: none"> <li>Corrosion results (rates, corrosion products, gas production ....). Siderite (FeCO<sub>3</sub>), Ankerite (CaFe(CO<sub>3</sub>)<sub>2</sub>) were identified by XRD and SEM/EDS.</li> </ol>	
Associates labs, funding organisation. JAEA.	<ol style="list-style-type: none"> <li>Iron compound added (e.g Fe, Fe<sub>3</sub>O<sub>4</sub>, Fe(II) solution....). Carbon Steel (&lt;0.02% C, &lt;0.35% Si, &lt;0.035% P, &lt;0.035% S, 0.6–1.2% Mn).</li> </ol>	<ol style="list-style-type: none"> <li>pH. Not controlled during experimental period.</li> </ol>	<ol style="list-style-type: none"> <li>Mineralogical results (reaction products, iron species, cementing effects ....). Mineralogical alteration of smectite was not identified. No iron smectite, such as nontronite and Fe-saponite, was detected by XRD.</li> </ol>	

Study – Basic information	Materials used	Experimental conditions	Results/Analyses	Documentation
			<p>TEM/EDS</p> <p>Typical lamella structure of phyllosilicate was observed.</p> <p>Fe concentration in this specimen was higher than that of starting smectite.</p>	
<p>4. Timing of study (start/end). Experiments started from 1996. 2003 for Analysis.</p>	<p>Type of iron compound (wire, coupon...).</p> <p>Fe-coupon: 30x30x2 mm.</p>	<p>6. Redox conditions (N<sub>2</sub>, Ar ....).</p> <p>N<sub>2</sub> Atmosphere (O<sub>2</sub> &lt; 1 ppm).</p>	<p>5. Physico-chemical properties (swelling pressure, CEC...).</p> <p>Bentonite kept the swelling ability after the experiment.</p>	
<p>5. Main objectives. To investigate the long-term behaviour of bentonite contacting with iron material.</p>	<p>5. Background electrolyte, other chemicals added. Synthetic seawater. (ASTM gradeD1141).</p>	<p>7. Type of experiments (batch, column, natural analogues....).</p> <p>Column type.</p>	<p>6. Conclusions from data/modelling. Precipitation of Fe was beared as carbonate. Fe exchanged for smectite interlayer cations. Mineralogical alteration of smectite was not identified. The bentonite kept swelling ability.</p>	
<p>6. Status of work (Jan 07). Completed.</p>		<p>8. Duration of test. 4 years.</p>		

## Iron-bentonite/smectite interactions – ongoing or planned study

Date: 31/01/07

Authors of this questionnaire: **Kenichi Ueno**

Responsible organisation: **JAEA**

Study – Basic information	Materials used	Experimental conditions	Results/Analyses	Documentation
1. Title of study. 2. Main investigator /organisation and e-mail. 3. Associates labs, funding organisation. 4. Timing of study (start/end). 5. Main objectives. 6. Status of work (Jan 07). 7. Planned work. 8. Info on modelling (approach, codes). 9. Other important info.	1. Type of bentonite/smectite. 2. Sample density (powder, compacted). 3. Iron compound added (e.g Fe, Fe <sub>3</sub> O <sub>4</sub> , Fe(II) solution....). 4. Type of iron compound (wire, coupon...). 5. Background electrolyte, other chemicals added.	1. Solid/liquid ratio. 2. Clay/Fe ratio. 3. Size of samples, volumes. 4. Temperature. 5. pH. 6. Redox conditions (N <sub>2</sub> , Ar ....). 7. Type of experiments (batch, column, natural analogues....). 8. Duration of test.	1. Analytical methods (solid, solution). 2. Corrosion results (rates, corrosion products, gas production ....). 3. Mineralogical results (reaction products, iron species, cementing effects ....). 4. Solution results (pH, solutes). 5. Physico-chemical properties (swelling pressure, CEC...). 6. Conclusions from data/modelling.	1. Unpublished reports. 2. Published reports. 3. Papers.
1. Title of study. Long-term (10 years) experiments for bentonite-iron interaction.	1. Type of bentonite/smectite. Kunigel V1.	3. Size of samples, volumes. Fe-coupon: 30x30x2 mm. Bentonite: 42 (diameter) x14 mm.	1. Analytical methods (solid, solution). Solid analysis. XRD, SEM/EDS, TEM/EDS,CEC, Exchangeable cations: extract by 1N- Ammonium acetate. Extracted cations measurement: Ca, Mg, Si, Fe measured by ICP Na, K measured by AAS. Solution analysis: NO.	
2. Main investigator /organisation and e-mail. Tadahiro SUYAMA, IDC Masahiro SHIBATA, JAEA Hiroshi SASAMOTO, JAEA Kenichi UENO, JAEA ueno.kenichi@jaea.go.jp	2. Sample density (powder, compacted). Compacted. Kunigel (dry density:1.8 g/cm <sup>3</sup> ). Kunigel 70%, Silica sand 30% (total dry density:1.6 g/cm <sup>3</sup> ).	4. Temperature. 50 (°C) 80 (°C).		



Study – Basic information	Materials used	Experimental conditions	Results/Analyses	Documentation
Associates labs, funding organisation. JAEA	3. Iron compound added (e.g Fe, Fe <sub>3</sub> O <sub>4</sub> , Fe(II) solution....).  SM400B(JIS G3202)  SFVC1(JIS G3106)	5. pH.  Not controlled during experimental period.		
4. Timing of study (start/end). 2006/2007 for Analysis. Experiments started from 1996.	Type of iron compound (wire, coupon...). Fe-coupon: 30x30x2 mm.	6. Redox conditions (N <sub>2</sub> , Ar ....). N <sub>2</sub> Atmosphere (O <sub>2</sub> < 1 ppm).		
5. Main objectives. To investigate the long-term behaviour of bentonite contacting with iron material.	5. Background electrolyte, other chemicals added. Synthetic seawater (ASTM grade D1141).	7. Type of experiments (batch, column, natural analogues....). Column type.		
6. Status of work (Jan 07). On going Analysing for bentonite parts.		8. Duration of test 10 years.		

## Iron-bentonite/smectite interactions – ongoing or planned study

Date: 31/01/07

Authors of this questionnaire: **Kenichi Ueno**

Responsible organisation: **JAEA**

Study – Basic information	Materials used	Experimental conditions	Results/Analyses	Documentation
1. Title of study. 2. Main investigator /organisation and e-mail. 3. Associates labs, funding organisation. 4. Timing of study (start/end). 5. Main objectives. 6. Status of work (Jan 07). 7. Planned work. 8. Info on modelling (approach, codes). 9. Other important info.	1. Type of bentonite/smectite. 2. Sample density (powder, compacted). 3. Iron compound added (e.g Fe, Fe <sub>3</sub> O <sub>4</sub> , Fe(II) solution....). 4. Type of iron compound (wire, coupon...). 5. Background electrolyte, other chemicals added.	1. Solid/liquid ratio. 2. Clay/Fe ratio. 3. Size of samples, volumes. 4. Temperature. 5. pH. 6. Redox conditions (N <sub>2</sub> , Ar ....). 7. Type of experiments (batch, column, natural analogues....). 8. Duration of test.	1. Analytical methods (solid, solution). 2. Corrosion results (rates, corrosion products, gas production ....). 3. Mineralogical results (reaction products, iron species, cementing effects ....). 4. Solution results (pH, solutes). 5. Physico-chemical properties (swelling pressure, CEC...). 6. Conclusions from data/modelling.	1. Unpublished reports. 2. Published reports. 3. Papers.
1. Title of study. Hydrothermal Experiments Using Fe-Bentonite.	1. Type of bentonite/smectite. Fe-bentonite preparation: Kunipia-F 7.5 g contacted with 1,500 ml 1M-FeCl <sub>2</sub> . After contacted FeCl <sub>2</sub> solution, three times washed by 80% ethanol. *Kunipia-F is a pure Na-bentonite.	1. Solid/liquid ratio. Solid/liquid ratio = 0.05 1.22(g)/25 ml (for 250°C). 5(g)/100 ml (for 150°C).	1. Analytical methods (solid, solution). Solution analysis: Ca, Mg, Si, Fe, Al: measured by ICP. Na, K: measured by AAS. Fe(II), total Fe: measured by colorimeters DR-2000. SO <sub>4</sub> <sup>2-</sup> : measured by Ion chromatography. Solid Analysis XRD SEM/EDS TEM/EDS CEC Exchangeable cations: extract by 1N-ammonium acetate. Ca, Mg, Si, Fe measured by ICP. Na, K measured by AAS.	2. Published reports. /Suyama et al. 2006/, JAEA-Research report, 2006-064. (for 250°C) (in Japanese). /Suyama et al. 2007/, JAEA-Research report, 2007-018. (for 150°C) (in Japanese). /M. Shibata et al. 2005/, "Experimental study on stability of iron (II) exchanged montmorillonite", 13th International clay Conference (ICC), Abstracts, p.116.

Study – Basic information	Materials used	Experimental conditions	Results/Analyses	Documentation
Associates labs, funding organisation. JAEA	3. Iron compound added (e.g Fe, Fe <sub>3</sub> O <sub>4</sub> , Fe(II) solution....). No. Initially FeCl <sub>2</sub> solution was supplied to prepare the starting materials (Fe-bentonite).	3. Size of samples, volumes. 25 ml 250°C. 100 ml 150°C.	3. Mineralogical results (reaction products, iron species, cementing effects ....).  XRD: Fe-bentonite was identified by XRD.  Small 0.7 nm non-expandable clay peak was detected by XRD (250°C, 6 months).  d(060) value of sample was 0.15 nm, which was characteristic of octahedral sheet.  The basal spacing of EG treated sample was 1.69 nm, which was a typical value for smectite.  TEM: 1.25 nm basal spacing of the smectite layer was observed.  No other minerals were observed.	
4. Timing of study (start/end) 2004/2006.	Type of iron compound (wire, coupon...). Powder.	4. Temperature. 250°C. 150°C.	4. Solution results (pH, solutes). Final solution pH. pH 6.1–6.7 (250°C, 1 months). pH 5.9–6.1 (250°C, 6 months). pH 5.1(150°C, 6 months). pH 5.7–6.0 (150°C, 20 months). Solutes: Fe(total) 5.9 mg/l. Fe(II) 5.5 mg/l (250°C, 6 months).	

Study – Basic information	Materials used	Experimental conditions	Results/Analyses	Documentation
<p>5. Main objectives.</p> <p>To investigate mineralogical change of Fe-bentonite at high temperature.</p>	<p>5. Background electrolyte, other chemicals added.</p> <p>No.</p> <p>Only add deionised water (25 ml).</p>	<p>5. pH.</p> <p>Not controlled for initial pH condition.</p>	<p>5. Physico-chemical properties (swelling pressure, CEC...).</p> <p>CEC:</p> <p>Decrease from starting materials.</p> <p>Amount of exchangeable cations (extract by 1N-ammonium acetate):</p> <p>Mg increased and Fe decreased after experiment.</p> <p>Increase of Mg might be caused by dissolution of initial smectite.</p> <p>Decrease of Fe might be caused by generation of secondary minerals.</p>	
<p>6. Status of work (Jan 07).</p> <p>Completed.</p>		<p>6. Redox conditions (N<sub>2</sub>, Ar ...).</p> <p>N<sub>2</sub> Atmosphere (O<sub>2</sub> &lt; 1 ppm).</p>	<p>6. Conclusions from data/modelling.</p> <p>No significant mineralogical change of smectite in this experimental condition.</p> <p>Small 0.7 nm non-expandable clay peak was detected by XRD. (250°C, 6 months).</p> <p>Most Fe-bentonite did not change to other minerals.</p>	
		<p>7. Type of experiments (batch, column, natural analogues...).</p> <p>Batch experiment in Au-tube (250°C).</p> <p>Batch experiment in Teflon-jar (150°C).</p>		
		<p>8. Duration of test.</p> <p>1 month, 6 months (250°C).</p> <p>12 month, 20 months (150°C).</p>		

## Iron-bentonite/smectite interactions – ongoing or planned study

Date: 17.1.2006

Authors of this questionnaire: **Antonín Vokál**

Responsible organisation: **NRI**

Study – Basic information	Materials used	Experimental conditions	Results/Analyses	Documentation
<ol style="list-style-type: none"> <li>Title of study.</li> <li>Main investigator/organisation and e-mail.</li> <li>Associates labs, funding organisation.</li> <li>Timing of study (start/end).</li> <li>Main objectives.</li> <li>Status of work (Jan 07).</li> <li>Planned work.</li> <li>Info on modelling (approach, codes).</li> <li>Other important info.</li> </ol>	<ol style="list-style-type: none"> <li>Type of bentonite/smectite.</li> <li>Sample density (powder, compacted).</li> <li>Iron compound added (e.g Fe, Fe<sub>3</sub>O<sub>4</sub>, Fe(II) solution....).</li> <li>Type of iron compound (wire, coupon...).</li> <li>Background electrolyte, other chemicals added.</li> </ol>	<ol style="list-style-type: none"> <li>Solid/liquid ratio.</li> <li>Clay/Fe ratio.</li> <li>Size of samples, volumes.</li> <li>Temperature.</li> <li>pH.</li> <li>Redox conditions (N<sub>2</sub>, Ar ....).</li> <li>Type of experiments (batch, column, natural analogues....).</li> <li>Duration of test.</li> </ol>	<ol style="list-style-type: none"> <li>Analytical methods (solid, solution).</li> <li>Corrosion results (rates, corrosion products, gas production ....).</li> <li>Mineralogical results (reaction products, iron species, cementing effects ....).</li> <li>Solution results (pH, solutes).</li> <li>Physico-chemical properties (swelling pressure, CEC...).</li> <li>Conclusions from data/modelling.</li> </ol>	<ol style="list-style-type: none"> <li>Unpublished reports.</li> <li>Published reports.</li> <li>Papers.</li> </ol>
<ol style="list-style-type: none"> <li>Study of corrosion of iron in contact with compacted bentonite – this is part of the work package “Study of corrosion of disposal canister materials and related processes in the project “Research of near field processes of DGR” funded by RAWRA.</li> </ol>	<ol style="list-style-type: none"> <li>Ca-Mg type of bentonite from deposit Rokle in Czech Republic.</li> </ol>	<ol style="list-style-type: none"> <li>Experiments are performed in diffusion cells with saturated compacted bentonite and iron powder. Different thickness of compacted bentonite layers are planned to be used (Now the first experiment is in progress).</li> </ol>	<ol style="list-style-type: none"> <li>X-ray diffraction, Raman spectroscopy analyses will be performed on corrosion products and bentonite after finishing experiments.</li> </ol>	<ol style="list-style-type: none"> <li>/Vokál et al./ Working reports of NRI for RAWRA (in Czech).</li> </ol>
<ol style="list-style-type: none"> <li>Antonín Vokál, Nuclear Research Institute Rez, voa@ujv.cz , Petr Bruha, Nuclear Research Institute Rez, brp@ujv.cz.</li> </ol>	<ol style="list-style-type: none"> <li>Different dry densities, in most of experiments: 1,600 kg/m<sup>3</sup>.</li> </ol>	<ol style="list-style-type: none"> <li>5 g of iron powder and a layer of compacted bentonite in the current experiment. Carbon steel electrodes and plates are used in electrochemical experiments and in some previous experiments.</li> </ol>	<ol style="list-style-type: none"> <li>Corrosion rate is determined from measuring of hydrogen evolution rates.</li> </ol>	<ol style="list-style-type: none"> <li>/Vokál A. et al./ Research of effect of corrosion products on carbon steel corrosion in bentonite environment, 3rd General Meeting and Workshop of NF-PRO Project, El Escorial, Spain, 14–16. November 2006.</li> </ol>
<ol style="list-style-type: none"> <li>Czech Technical University is associated laboratory; RAWRA and Ministry of Trade</li> </ol>	<ol style="list-style-type: none"> <li>Iron powder.</li> </ol>	<ol style="list-style-type: none"> <li>Thickness of compacted bentonite about 10 to 15 mm, diameter 10 mm.</li> </ol>	<ol style="list-style-type: none"> <li>X-ray diffraction and Raman spectroscopy will be performed on bentonite samples</li> </ol>	<ol style="list-style-type: none"> <li>/Vokál 2006/ Carbon Steel Canister Performance Assessment:</li> </ol>

Study – Basic information	Materials used	Experimental conditions	Results/Analyses	Documentation
and Industry are main funding institutions. Part of the activities is also supported by EC in the framework of NF-PRO project.			and iron corrosion products (in previous experiments mainly magnetite and goethite were identified by X-ray diffraction with increasing content of magnetite with time of corrosion).	Iron Transfer Study, Materials Research Society Symp. Proc. 932, Ed, P. Van Iseghem, p. 877, 2006.
4. 2004–2008.	4. Iron powder and carbon steel plates and rods.	4. Different temperatures (now mainly 80°C for an acceleration of corrosion rates).	4. Will be performed.	
5. To establish scientific basis for performance assessments of deep geological repository in the Czech Republic.	5. In the first experiments bentonite pore water for Volclay Na-bentonite developed in PSI in the framework of NF-PRO project was used, In the experiments with Ca-Mg bentonite 0.1 M CaCl <sub>2</sub> solution is used, porewater composition of the Ca-Mg bentonite is under development.	5. pH about 8 (bentonite pore water).	5. Swelling pressure of bentonite in contact with iron powder at 80 °C will be measured in special equipment now under preparation.	
6. Under way. Corrosion of iron in contact with compacted bentonite in diffusion cells with measuring hydrogen evolution.		6. N <sub>2</sub> .	6. The most of corrosion experiments have been performed only in bentonite and distilled water so far. Now experiments of corrosion of iron powder in contact with compacted bentonite started. The first experiment is still under way. It will be finished in some weeks and compacted bentonite and corrosion products will be analysed. The first results suggest that the hydrogen penetrates after some time without problems through a thin layer of compacted bentonite.	

Study – Basic information	Materials used	Experimental conditions	Results/Analyses	Documentation
7. The first experiment with a thin layer of bentonite is in progress, further experiments will continue after evaluation of the first experiment.		7. Experiments in diffusion cells in special NRI made equipment enabling to measure hydrogen evolution.		
8. GoldSim Transport code for iron species transport calculations and PHREEQC calculations.		8. Long-term experiments until pseudo steady state (months).		

## Iron-bentonite/smectite interactions – ongoing or planned study

Date: 17.1.2006

Authors of this questionnaire: **Antonín Vokál**

Responsible organisation: **NRI**

Study – Basic information	Materials used	Experimental conditions	Results/Analyses	Documentation
<ol style="list-style-type: none"> <li>Title of study.</li> <li>Main investigator/ organisation and e-mail.</li> <li>Associates labs, funding organisation.</li> <li>Timing of study (start/end).</li> <li>Main objectives.</li> <li>Status of work (Jan 07).</li> <li>Planned work.</li> <li>Info on modelling (approach, codes).</li> <li>Other important info.</li> </ol>	<ol style="list-style-type: none"> <li>Type of bentonite/ smectite.</li> <li>Sample density (powder, compacted).</li> <li>Iron compound added (e.g Fe, Fe<sub>3</sub>O<sub>4</sub>, Fe(II) solution....).</li> <li>Type of iron compound (wire, coupon...).</li> <li>Background electrolyte, other chemicals added.</li> </ol>	<ol style="list-style-type: none"> <li>Solid/liquid ratio.</li> <li>Clay/Fe ratio.</li> <li>Size of samples, volumes.</li> <li>Temperature.</li> <li>pH.</li> <li>Redox conditions (N<sub>2</sub>, Ar ....).</li> <li>Type of experiments (batch, column, natural analogues....).</li> <li>Duration of test.</li> </ol>	<ol style="list-style-type: none"> <li>Analytical methods (solid, solution).</li> <li>Corrosion results (rates, corrosion products, gas production ....).</li> <li>Mineralogical results (reaction products, iron species, cementing effects ....).</li> <li>Solution results (pH, solutes).</li> <li>Physico-chemical properties (swelling pressure, CEC...).</li> <li>Conclusions from data/modelling.</li> </ol>	<ol style="list-style-type: none"> <li>Unpublished reports.</li> <li>Published reports.</li> <li>Papers.</li> </ol>
<ol style="list-style-type: none"> <li>Electrochemical Noise Analyses and other electrochemical studies of corrosion of carbon steel in bentonite environment - this is part of work package "Study of corrosion of disposal canister materials and related processes" in the project "Research of near field processes of DGR" funded by RAWRA.</li> </ol>	<ol style="list-style-type: none"> <li>Ca-Mg type of bentonite from deposit Rokle in Czech Republic.</li> </ol>	<ol style="list-style-type: none"> <li>The current experiments are performed in corrosion cells with bentonite water.</li> </ol>	<ol style="list-style-type: none"> <li>Common analyses will be performed on corrosion products after finishing experiments (X-ray diffraction, Raman, Metalography for some samples).</li> </ol>	<ol style="list-style-type: none"> <li>/Vokál et al. Working reports of NRI for RAWRA (in Czech).</li> </ol>
<ol style="list-style-type: none"> <li>Antonín Vokál, Nuclear Research Institute Rez, voa@ujv.cz. Rostislav Silber, Nuclear Research Institute Rez, sil@ujv.cz. David Dobrev, Nuclear Research Institute Rez, dob@ujv.cz.</li> </ol>	<ol style="list-style-type: none"> <li>The first experiments are performed in bentonite water, but further experiment will be performed in bentonite suspension and then in compacted bentonite.</li> </ol>	<ol style="list-style-type: none"> <li>Will be determined, Now only experiments in bentonite water are in progress.</li> </ol>	<ol style="list-style-type: none"> <li>Corrosion rate is determined from measuring of hydrogen evolution rates and will be compared with electrochemical measurements.</li> </ol>	<ol style="list-style-type: none"> <li>/Vokál et al./ Research of effect of corrosion products on carbon steel corrosion in bentonite environment, 3rd General Meeting and Workshop of NF-PRO Project, El Escorial, Spain, 14–16. November 2006.</li> </ol>



Study – Basic information	Materials used	Experimental conditions	Results/Analyses	Documentation
3. Czech Technical University is associated laboratory; RAWRA and Ministry of Trade and Industry are main funding institutions. Part of the activities is also supported by EC in the framework of NF-PRO project.	3. Iron powder.	5. Carbon steel electrodes, volume of corrosion cell about 1 l.	3. X-ray diffraction and Raman spectroscopy will be performed on bentonite samples and iron corrosion products. Metalography will be performed on carbon steels.	
4. 2005– 2008.	4. Carbon steel electrodes.	4. Different temperatures.		
5. Concrete objective of the study: to study the nature of corrosion products and corrosion processes on the surface of carbon steels in contact with bentonite.	5. In the first experiments bentonite pore water for Vol-clay Na-bentonite developed in PSI in the framework of NF-PRO project was used, In further experiments with Ca-Mg bentonite 0.1 M CaCl <sub>2</sub> solution is used, porewater composition of the Ca-Mg bentonite is under development.	5. pH about 8 (bentonite pore water).		
6. Under way – Experiments in bentonite water.		6. N <sub>2</sub> .	6. The experiments have been performed in bentonite and distilled water. It was found that electrochemical noise analyses can monitor corrosion processes of carbon steel in bentonite environment. These experiment can help to understand the corrosion processes occurring on the surface of carbon steel in contact with bentonite.	
7. Electrochemical analyses of carbon steel corrosion in contact with bentonite suspension and then with compacted bentonite.				
		8. Weeks.		

## Iron-bentonite/smectite interactions – ongoing or planned study

Date: 17.1.2006

Authors of this questionnaire: **Antonín Vokál**

Responsible organisation: **NRI**

Study – Basic information	Materials used	Experimental conditions	Results/Analyses	Documentation
<ol style="list-style-type: none"> <li>1. Title of study.</li> <li>2. Main investigator/ organisation and e-mail.</li> <li>3. Associates labs, funding organisation.</li> <li>4. Timing of study (start/end).</li> <li>5. Main objectives.</li> <li>6. Status of work (Jan 07).</li> <li>7. Planned work.</li> <li>8. Info on modelling (approach, codes).</li> <li>9. Other important info.</li> </ol>	<ol style="list-style-type: none"> <li>1. Type of bentonite/ smectite.</li> <li>2. Sample density (powder, compacted).</li> <li>3. Iron compound added (e.g Fe, Fe<sub>3</sub>O<sub>4</sub>, Fe(II) solution....).</li> <li>4. Type of iron compound (wire, coupon...).</li> <li>5. Background electrolyte, other chemicals added.</li> </ol>	<ol style="list-style-type: none"> <li>1. Solid/liquid ratio.</li> <li>2. Clay/Fe ratio.</li> <li>3. Size of samples, volumes.</li> <li>4. Temperature.</li> <li>5. pH.</li> <li>6. Redox conditions (N<sub>2</sub>, Ar ....).</li> <li>7. Type of experiments (batch, column, natural analogues....).</li> <li>8. Duration of test.</li> </ol>	<ol style="list-style-type: none"> <li>1. Analytical methods (solid, solution).</li> <li>2. Corrosion results (rates, corrosion products, gas production ....).</li> <li>3. Mineralogical results (reaction products, iron species, cementing effects ....).</li> <li>4. Solution results (pH, solutes).</li> <li>5. Physico-chemical properties (swelling pressure, CEC...).</li> <li>6. Conclusions from data/modelling.</li> </ol>	<ol style="list-style-type: none"> <li>1. Unpublished reports.</li> <li>2. Published reports.</li> <li>3. Papers.</li> </ol>
<ol style="list-style-type: none"> <li>1. Study of migration of iron in compacted bentonite and the effect of iron and iron corrosion products on sorption of selected radionuclides on bentonite – this is part of work package "Study of migration of radionuclides and relevant chemical processes" in the project "Research of near field processes of DGR" funded by RAWRA – this study will start this year.</li> </ol>	<ol style="list-style-type: none"> <li>1. Ca-Mg type of bentonite from deposit Rokle in Czech Republic after removing iron from bentonite.</li> </ol>	<ol style="list-style-type: none"> <li>1. The diffusion experiments will be performed in special diffusion cells made of PEEK with saturated bentonite with iron powder or iron plates.  Sorption experiment will be performed by methodology.</li> </ol>	<p>Spectroscopy methods to determine iron concentration in bentonite ,X-ray diffraction of analyses of solid bentonite.</p> <p>Common sorption methodology analyses.</p>	<ol style="list-style-type: none"> <li>1. /Vokál et al. Working reports of NRI for RAWRA (in Czech).</li> </ol>
<ol style="list-style-type: none"> <li>2. Antonín Vokál, Nuclear Research Institute Rez, voa@ujv.cz  Jan Vejsada, Nuclear Research Institute Rez, vsd@ujv.cz</li> </ol>				

Study – Basic information	Materials used	Experimental conditions	Results/Analyses	Documentation
3. Czech Technical University is associated laboratory; RAWRA and Ministry of Trade and Industry are main funding institutions. Part of the activities is also supported by EC in the framework of NF-PRO project.				3. /Vejsada 2006/ The uncertainties associated with the application of batch technique for distribution coefficients determination – a case study of cesium adsorption on four different bentonites, Applied Radiation and Isotopes, Vol. 64 (2006), 1538–1548.  /Vejsada 2006/: Study of caesium sorption on Na and Ca-Mg bentonites using batch and diffusion experiments, Czechoslovak Journal of Physics, Vol. 56 (2006), Suppl. D, D73-D80.
4. 2007–2008	Iron powder	4.	4.	
5. To study diffusion of iron in bentonite and determine sorption capacity of bentonite in contact with iron and iron corrosion products.	5. In the first experiments bentonite pore water for Volclay Na-bentonite developed in PSI in the framework of NF-PRO project was used, In further experiments with Ca-Mg bentonite 0.1 M CaCl <sub>2</sub> solution is used, porewater composition of the Ca-Mg bentonite is under development.	5. pH about 8 (bentonite pore water).	5.	
6. N <sub>2</sub> .				

## Iron-bentonite/smectite interactions – ongoing or planned study

Date: May 2007

Authors of this questionnaire: **David Savage**

Responsible organisation: **Quintessa**

Study – Basic information	Materials used	Experimental conditions	Results/Analyses	Documentation
<ol style="list-style-type: none"> <li>1. Title of study.</li> <li>2. Main investigator/organisation and e-mail.</li> <li>3. Associates labs, funding organisation.</li> <li>4. Timing of study (start/end).</li> <li>5. Main objectives.</li> <li>6. Status of work (Jan 07).</li> <li>7. Planned work.</li> <li>8. Info on modelling (approach, codes).</li> <li>9. Other important info.</li> </ol>	<ol style="list-style-type: none"> <li>1. Type of bentonite/smectite.</li> <li>2. Sample density (powder, compacted).</li> <li>3. Iron compound added (e.g Fe, Fe<sub>3</sub>O<sub>4</sub>, Fe(II) solution....).</li> <li>4. Type of iron compound (wire, coupon...).</li> <li>5. Background electrolyte, other chemicals added.</li> </ol>	<ol style="list-style-type: none"> <li>1. Solid/liquid ratio.</li> <li>2. Clay/Fe ratio.</li> <li>3. Size of samples, volumes.</li> <li>4. Temperature.</li> <li>5. pH.</li> <li>6. Redox conditions (N<sub>2</sub>, Ar ....).</li> <li>7. Type of experiments (batch, column, natural analogues....).</li> <li>8. Duration of test.</li> </ol>	<ol style="list-style-type: none"> <li>1. Analytical methods (solid, solution).</li> <li>2. Corrosion results (rates, corrosion products, gas production ....).</li> <li>3. Mineralogical results (reaction products, iron species, cementing effects ....).</li> <li>4. Solution results (pH, solutes).</li> <li>5. Physico-chemical properties (swelling pressure, CEC...).</li> <li>6. Conclusions from data/modelling.</li> </ol>	<ol style="list-style-type: none"> <li>1. Unpublished reports.</li> <li>2. Published reports.</li> <li>3. Papers.</li> </ol>
<ol style="list-style-type: none"> <li>1. Interaction of iron with bentonite.</li> </ol>	<ol style="list-style-type: none"> <li>1. MX-80.</li> </ol>	<p>N/A</p>	<ol style="list-style-type: none"> <li>6. Results of AMBER modelling agree with those of Vokal et al. (Materials Research Society, 2005).</li> </ol> <p>Testing of QPAC against experimental results of Wilkin and Barnes (American Mineral. 2000) show good agreement for crystal growth and particle size distributions.</p> <p>Preliminary literature survey suggests that clay transformation will be dominated by Ostwald step processes.</p>	<ol style="list-style-type: none"> <li>1. Unpublished Quintessa data.</li> </ol>
<ol style="list-style-type: none"> <li>2. David Savage, Claire Watson, David Hodgkinson, Sarah Watson.</li> </ol> <p>Quintessa Limited, Henley-on-Thames, UK.</p> <p>daidsavage@quintessa.org</p>	<ol style="list-style-type: none"> <li>2. Dry density = 1.6 MG/m<sup>3</sup>.</li> </ol>			<ol style="list-style-type: none"> <li>2. NF-Pro reports to be completed end-2007.</li> </ol>

Study – Basic information	Materials used	Experimental conditions	Results/Analyses	Documentation
3. EC NF-Pro Project, co-funded by EC and UK Nirex Ltd (Simon Norris).	3. Iron canister.			3. Abstract submitted to Lund Clay Workshop planned for Nov 2007.
4. Jan 2004– Dec 2007.	4. Iron canister.			
5. To model corrosion of iron canister, diffusion and transport of iron through bentonite, and long-term alteration of the clay.	5. Not decided.			
6. Preliminary modelling of iron corrosion and transport of Fe through bentonite using the Quintessa compartment code, AMBER has been completed.  Development of the Quintessa performance assessment code, QPAC to include processes of nucleation, precursor cannibalisation, and Ostwald ripening (as described by Steefel and van Cappellen, 1990) has been completed and successfully tested against experimental data for zeolite growth.				
7. Application of QPAC to the iron-bentonite system will commence in the next quarter of 2007.  Natural systems data will be reviewed to incorporate appropriate secondary minerals in the modelled system.				
8. The modelling work will be conducted using QPAC.				
9.				

## Questionnaire: Iron-bentonite/smectite interactions – ongoing or planned study

Date: 8 February 2007

Authors of this questionnaire: **Nick R. Smart**

Responsible organisation: **Serco Assurance**

Study – Basic information	Materials used	Experimental conditions	Results/Analyses	Documentation
<ol style="list-style-type: none"> <li>Title of study.</li> <li>Main investigator/organisation and e-mail.</li> <li>Associates labs, funding organisation.</li> <li>Timing of study (start/end).</li> <li>Main objectives.</li> <li>Status of work (Jan 07).</li> <li>Planned work.</li> <li>Info on modelling (approach, codes).</li> <li>Other important info.</li> </ol>	<ol style="list-style-type: none"> <li>Type of bentonite/smectite.</li> <li>Sample density (powder, compacted).</li> <li>Iron compound added (e.g Fe, Fe<sub>3</sub>O<sub>4</sub>, Fe(II) solution....).</li> <li>Type of iron compound (wire, coupon...).</li> <li>Background electrolyte, other chemicals added.</li> </ol>	<ol style="list-style-type: none"> <li>Solid/liquid ratio.</li> <li>Clay/Fe ratio.</li> <li>Size of samples, volumes.</li> <li>Temperature.</li> <li>pH.</li> <li>Redox conditions (N<sub>2</sub>, Ar ....).</li> <li>Type of experiments (batch, column, natural analogues....).</li> <li>Duration of test.</li> </ol>	<ol style="list-style-type: none"> <li>Analytical methods (solid, solution).</li> <li>Corrosion results (rates, corrosion products, gas production ....).</li> <li>Mineralogical results (reaction products, iron species, cementing effects ....).</li> <li>Solution results (pH, solutes).</li> <li>Physico-chemical properties (swelling pressure, CEC...).</li> <li>Conclusions from data/modelling.</li> </ol>	<ol style="list-style-type: none"> <li>Unpublished reports.</li> <li>Published reports.</li> <li>Papers.</li> </ol>
<p>Anaerobic corrosion of iron in bentonite.</p> <p>Nick Smart, Serco Assurance, nick.smart@serco.com.</p> <p>Collaboration with Posiva, GSF, SKB, Clay technology. Funded by SKB and EU (NF-PRO project).</p> <p>Start: ~2001; still in progress.</p> <p>To characterise (i) the corrosion rates and corrosion products of anaerobically corroding iron, and (ii) the physico-chemical properties of bentonite in contact with corroding iron. Also chemical modelling work in support of analysis of experimental data.</p>	<ol style="list-style-type: none"> <li>MX-80.</li> <li>Most experiments in compacted bentonite. A few experiments in slurry.</li> <li>Corroding carbon steel, cast iron and stainless steel.</li> <li>As above.</li> <li>Artificial groundwater (e.g. Allard) and NaCl solutions, pH 8.4 and 11.</li> </ol>	<p>30 wt% bentonite in water slurry and compacted bentonite immersed in test solution.</p> <p>Coupons in compacted bentonite or wire:bentonite</p> <p>Approximately 15,300 wires were added to the test cell, which gives a total surface area of about 0.1 m<sup>2</sup>, a volume of about 9.6 cm<sup>3</sup> and a mass of around 75 g. The iron wires were added to bentonite prior to compaction of the samples and the wires were fairly evenly distributed within the samples. The test cell volume was ~42 cm<sup>3</sup>, of which compacted bentonite (MX-80, 2 g/cm<sup>3</sup>) formed about 32.3 cm<sup>3</sup> (64.6 g).</p>	<p>Analysis of solid only.</p> <p>SEM-EDX and EMPA, laser Raman spectroscopy, anoxic XRD and Mössbauer spectroscopy, oxic XRD, FTIR, TEM-EDS, CEC and exchangeable cations and total chemical composition.</p> <p>Rates, corrosion product identification, gas production.</p> <p>Analysed supernatant of bentonite equilibrated with artificial groundwater.</p> <p>Swelling pressure, hydraulic conductivity.</p> <p>Transport is restricted by sorption and/or complexation.</p>	<p>N.R. Smart, A.P. Rance &amp; L.O. Werme, Anaerobic Corrosion of Steel in Bentonite presented at MRS 2003, Kalmar, Sweden, June 15–18, 2003, Materials Research Society Symposium Proceedings Volume 807, Scientific Basis for Nuclear Waste Management XXVII, V.M. Oversby and L.O. Werme (eds.), p. 441–446, 2004. L. Carlson, O. Karland, V.M. Oversby, A..P. Rance, N.R. Smart, M. Snellman, M. Vähänen &amp; L.O. Werme Experimental Studies of the Interactions Between Anaerobically Corroding Iron and Bentonite, presented at conference on Clays in Natural and Engineered Barriers for Waste</p>

Study – Basic information	Materials used	Experimental conditions	Results/Analyses	Documentation
<p>Work is ongoing. NF-PRO ends in December 2007. Experiments and modelling will continue after 2007.</p> <p>Continue corrosion rate measurements. Complete analysis of bentonite. Expand modelling.</p> <p>PHREEQC used to model equilibrium porewater compositions and mass transport of iron in bentonite.</p>		<p>6. See above 30 °C and 50°C.</p> <p>External pH to compacted bentonite 8.4 and 11.</p> <p>Anoxic – set up and sealed in nitrogen.</p> <p>Steel/bentonite compacted in stainless steel holder and mounted in sealed glass cell.</p> <p>Longest 911 days.</p>		<p>Confinement, held in Tours, France, March 14–18, 2005, Physics and Chemistry of the Earth, to be published, 2006. N.R. Smart, A.P. Rance, L. Carlson and L.O. Werme, Further Studies of the Anaerobic Corrosion of Steel in Bentonite presented at MRS 2005, Ghent, 2005, Mat. Res Soc. Symp. Proc 932, 813, 2006. L. Carlson, O. Karnland. S. Olsson, A.P. Rance and N.R. Smart, Experimental Studies on the Interactions Between Anaerobically Corroding Iron and Bentonite, Posiva Working Report 2006-60, 2006. N.R. Smart, L. Carlson, F.M.I. Hunter, O. Karnland, A.M. Pritchard, A.P. Rance and L.O. Werme, Interactions Between Iron Corrosion Products and Bentonite, SA/EIG/12156/ C001, 2006 (NF-PRO .progress report (Serco Assurance report).</p>

## Iron-bentonite/smectite interactions – ongoing or planned study

Date: 15/05/07

Authors: **Laurent Charlet**

Responsible organisation: **University of Grenoble-I (UJF) /ANDRA**

Study – Basic information	Materials used	Experimental conditions	Results/Analyses	Documentation
<ol style="list-style-type: none"> <li>1. Title of study.</li> <li>2. Main investigator/ organisation and e-mail.</li> <li>3. Associates labs, funding organisation.</li> <li>4. Timing of study (start/end).</li> <li>5. Main objectives.</li> <li>6. Status of work (Jan 07).</li> <li>7. Planned work.</li> <li>8. Info on modelling (approach, codes).</li> <li>9. Other important info.</li> </ol>	<ol style="list-style-type: none"> <li>1. Type of bentonite/ smectite.</li> <li>2. Sample density (powder, compacted).</li> <li>3. Iron compound added (e.g Fe, Fe<sub>3</sub>O<sub>4</sub>, Fe(II) solution....).</li> <li>4. Type of iron compound (wire, coupon...).</li> <li>5. Background electrolyte, other chemicals added.</li> </ol>	<ol style="list-style-type: none"> <li>1. Solid/liquid ratio.</li> <li>2. Clay/Fe ratio.</li> <li>3. Size of samples, volumes.</li> <li>4. Temperature.</li> <li>5. pH.</li> <li>6. Redox conditions (N<sub>2</sub>, Ar ....).</li> <li>7. Type of experiments (batch, column, natural analogues....).</li> <li>8. Duration of test.</li> </ol>	<ol style="list-style-type: none"> <li>1. Analytical methods (solid, solution)</li> <li>2. Corrosion results (rates, corrosion products, gas production ....).</li> <li>3. Mineralogical results (reaction products, iron species, cementing effects ....).</li> <li>4. Solution results (pH, solutes).</li> <li>5. Physico-chemical properties (swelling pressure, CEC...).</li> <li>6. Conclusions from data/modelling.</li> </ol>	<ol style="list-style-type: none"> <li>1. Unpublished reports.</li> <li>2. Published reports.</li> <li>3. Papers.</li> </ol>
<p>Electron transfer at the mineral/water interface: Selenium reduction by ferrous iron” Charlet, Laurent.charlet@obs.ujf-grenoble.fr UJF-Grenoble, France Completed in 06 modeling: DFT (molecular modeling) and MUSIC (surface complexation).</p>	<p>Synthetic Fe-free montmorillonite.</p>	<p>2 g/L clay. 0.05 M CaCl<sub>2</sub> ionic background. N<sub>2</sub> glovebox. Batch. 1 month.</p>	<p>1. Analysis of solid only. SEM-EDX and EMPA, laser Raman spectroscopy, anoxic XRD and Mössbauer spectroscopy, oxic XRD, FTIR, TEM-EDS, CEC and exchangeable cations and total chemical composition.</p>	<p>Electron transfer at the mineral/water interface: Selenium reduction by ferrous iron.  GCA /Charlet et al. 2007/ In review.</p>
<p>Reversible surface-sorption-induced electron-transfer oxidation of Fe(II) at reactive sites on a synthetic clay mineral.  Laurent Charlet laurent.charlet@obs.ujf-grenoble.fr. Completed in 06, published in 07.</p>	<p>Synthetic Fe-free montmorillonite.</p>	<p>2 g/L clay. 0.05 M CaCl<sub>2</sub> ionic background. N<sub>2</sub> glovebox. Batch.</p>	<p>Fe<sup>2+</sup> affinity for montmorillonite edge sites (complexation constants 2 –3 levels of magnitude larger to that observed for other divalent transition metal ions) Fe(II) oxidation occurs on the edge and is fully reversible. It increases as pH increases and decreases as pH decrease.  The oxidant/reductant is water/ adsorbed hydrogen, respectively</p>	<p>/Géhin 2007/ Reversible surface-sorption-induced electron-transfer oxidation of Fe(II) at reactive sites on a synthetic clay mineral Geochimica et Cosmochimica Acta 71 863–876.</p>



Study – Basic information	Materials used	Experimental conditions	Results/Analyses	Documentation
<p>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.</p> <p>Charlet and Tournassat laurent.charlet@obs.ujf-grenoble.fr</p>	Synthetic Fe-free montmorillonite.	<p>2 g/L clay suspension</p> <p>0.05 M CaCl<sub>2</sub> ionic background</p> <p>N<sub>2</sub> glovebox</p> <p>Batch</p>	<p>As exchangeable cations on montmorillonite, Fe<sup>2+</sup> behaves like Ca<sup>2+</sup> (K<sub>v</sub> = 1.0).</p> <p>The CaCl<sup>+</sup> ion pair has a very high affinity.</p>	<p>/Charlet and Tournassat 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 Aqueous Geochemistry 11:115-137.</p>
<p>Reduction of selenium by green rust and siderite</p> <p>L. Charlet and A. Scheinost laurent.charlet@obs.ujf-grenoble.fr and Scheinost@esrf.fr</p>	Green rust, magnetite and siderite.	<p>N<sub>2</sub> glovebox.</p> <p>Batch.</p>	<p>Reduction of Se to Se(-I) or Se(-II), depending on the solid phase.</p>	<p>/Scheinost and Charlet/ ESTsubmitted.</p>
<p>Reduction of U(VI) by montmorillonite surface and structural Fe(II).</p> <p>Laurent Charlet and Fabienne Favre. On going study. laurent.charlet@obs.ujf-grenoble</p>	Natural smectites with different amounts of structural Fe(II) band different type of substitution, as well as synthetic montmorillonites with different levels of Fe(II) substitution.	<p>2 g/L clay suspension.</p> <p>0.05 M CaCl<sub>2</sub> ionic background.</p> <p>N<sub>2</sub> glovebox.</p> <p>Batch.</p>	<p>Expected result: reduction of U to U(IV) (same as Liger et al. 1999 Geochim. Cosmochim. Acta 19/20, 2939-2956).</p>	
<p>Reduction of Pu (V or VI) by Fe(II) in presence of montmorillonite.</p> <p>Andreas Scheinost, Laurent Charlet + Regina Kirsch (PhD student) scheinost@esrf.fr Start: May 2007</p>	Synthetic Fe-free montmorillonite.	<p>2 g/L clay suspension.</p> <p>0.05 M CaCl<sub>2</sub> ionic background.</p> <p>N<sub>2</sub> glovebox.</p> <p>Batch.</p>	<p>None yet.</p>	
<p>Adsorption of Fe(II) on natural montmorillonite</p> <p>Completed C. Tournassat@brgm.fr</p>	MX80.	<p>2 g/L clay suspension.</p> <p>0.05 M CaCl<sub>2</sub> ionic background.</p> <p>N<sub>2</sub> glovebox.</p> <p>Batch.</p>	<p>Confirmation of results obtained with pure Fe-free montmorillonite (see above, /Géhin et al. 2007/.</p>	<p>/Tournassat 2007/. Interactions of metals and H<sub>4</sub>SiO<sub>4</sub> at clay/water interface. Part I. Fe(II) high affinity for natural montmorillonite and implications in anoxic and iron-rich systems modelling. Geochimica et Cosmochimica Acta (under review).</p>

Study – Basic information	Materials used	Experimental conditions	Results/Analyses	Documentation
Mössbauer evidence of the Fe(II) high redox reactivity in clay phases of Callovo-Oxfordian clay-stones. Implications for sample transport and preservation.	Callovian-Oxfordian clay-stone.		Mössbauer evidence of Fe(II) high reactivity (e.g. to variation of temperature).	Mössbauer evidence of the Fe(II) high redox reactivity in clay phases of Callovian-Oxfordian clay-stones. Implications for sample transport and preservation.  /Tourmassat et al. 2007/.  1st. Annual Workshop Proceedings 6 <sup>TH</sup> EC FP - FUNMIG IP.  Saclay (France) 28 <sup>th</sup> Nov.– 1 <sup>st</sup> . Dec. 2005.
Cooperative sorption of Fe(II), Co(II) and Eu(III) and silicic acid on montmorillonite.  Charlet, Géhin, Tourmassat et al.  laurent.charlet@obs.ujf-grenoble  Completed in 2006.	MX 80.	2 g/L clay suspension.  0.05 M CaCl <sub>2</sub> ionic background.  N <sub>2</sub> glovebox.  Batch.	Mossbauer and chemical analyses.  Fe(II), even strongly adsorbed on edges, cannot desorb Co and Eu. On the contrary, a cooperative adsorption is observed, with co-adsorption of silicic acid, particularly with Co.	/Géhin, Wolthers, Charlet/ Cooperative sorption of Fe(II), Co(II) and Eu(III) and silicic acid on montmorillonite. Geochimica Cosmochimica Acta (in prep.)
Interactions of metals and H <sub>4</sub> SiO <sub>4</sub> at clay/water interface. Competitive Fe sorption vs. surface precipitation or surface oxidation on natural montmorillonite.  C.Tourmassat@brgm.fr  Tourmassat, Charlet, Géhin.  Completed.	MX 80	2 g/L clay suspension.  0.05 M CaCl <sub>2</sub> ionic background.  N <sub>2</sub> glovebox.  Batch.	Mossbauer and chemical analyses.  Pending results.	/Tourmassat 2007/. Interactions of metals and H <sub>4</sub> SiO <sub>4</sub> at clay/water interface. Competitive Fe sorption vs. surface precipitation or surface oxidation on natural montmorillonite. Geochimica et Cosmochimica Acta (under review).

## Iron-bentonite/smectite interactions – ongoing or planned study

Date: 16/07/07

Authors of this questionnaire: **Bertrand Fritz**

Responsible organisation: **CGS, CNRS-ULP, Strasbourg, France**

Study – Basic information	Materials used	Experimental conditions	Results/Analyses	Documentation
<ol style="list-style-type: none"> <li>Title of study.</li> <li>Main investigator/organisation and e-mail.</li> <li>Associates labs, funding organisation.</li> <li>Timing of study (start/end).</li> <li>Main objectives.</li> <li>Status of work (Jan 07).</li> <li>Planned work.</li> <li>Info on modelling (approach, codes).</li> <li>Other important info.</li> </ol>	<ol style="list-style-type: none"> <li>Type of bentonite/smectite.</li> <li>Sample density (powder, compacted).</li> <li>Iron compound added (e.g Fe, Fe<sub>3</sub>O<sub>4</sub>, Fe(II) solution....).</li> <li>Type of iron compound (wire, coupon...).</li> <li>Background electrolyte, other chemicals added.</li> </ol>	<ol style="list-style-type: none"> <li>Solid/liquid ratio.</li> <li>Clay/Fe ratio.</li> <li>Size of samples, volumes.</li> <li>Temperature.</li> <li>pH.</li> <li>Redox conditions (N<sub>2</sub>, Ar ....).</li> <li>Type of experiments (batch, column, natural analogues....).</li> <li>Duration of test.</li> </ol>	<ol style="list-style-type: none"> <li>Analytical methods (solid, solution).</li> <li>Corrosion results (rates, corrosion products, gas production ....).</li> <li>Mineralogical results (reaction products, iron species, cementing effects ....).</li> <li>Solution results (pH, solutes).</li> <li>Physico-chemical properties (swelling pressure, CEC...).</li> <li>Conclusions from data/modelling.</li> </ol>	<ol style="list-style-type: none"> <li>Unpublished reports.</li> <li>Published reports.</li> <li>Papers.</li> </ol>
<ol style="list-style-type: none"> <li>Iron – Clay interactions in bentonite barriers: theoretical study and numerical modelling.</li> </ol>	<ol style="list-style-type: none"> <li>MX-80.</li> </ol>	<ol style="list-style-type: none"> <li>1.56 (volumes).</li> </ol>	<ol style="list-style-type: none"> <li>Simulated data.</li> </ol>	<ol style="list-style-type: none"> <li>D. Sali (PhD,ULP Strasbourg, 2003), N. Marty (PhD, ULP Strasbourg, 2006).</li> </ol>
<ol style="list-style-type: none"> <li>B. Fritz, CGS, CNRS-ULP, bfritz@illite.u-strasbg.fr</li> </ol>	<ol style="list-style-type: none"> <li>1.6 g/cm<sup>3</sup>.</li> </ol>	<ol style="list-style-type: none"> <li>Fe (Fe<sup>2+</sup>) due to the diffusion from the corroded steel overpack, through the clay phase.</li> </ol>	<ol style="list-style-type: none"> <li>Between 5 μm.year<sup>-1</sup> initially and 0.2 μm.year<sup>-1</sup>.</li> </ol>	<ol style="list-style-type: none"> <li>Contract reports AND ANDRA C.RP. 0 CGS 04-001 :. 44 p. ANDRA C.RP. 0 CGS 05-001, 50p. ANDRA C.RP. 0 CGS 05-002,34p. + annexes.</li> </ol>
<ol style="list-style-type: none"> <li>Cooperation: G2R and LEM, Nancy funding : ANDRA, Chatenay-Malabry, France.</li> </ol>	<ol style="list-style-type: none"> <li>Corrosion of iron, aqueous Fe(II).</li> </ol>	<ol style="list-style-type: none"> <li>1 m length of clay barrier (section :5 x 5 cm) in 20 cells (5 cm length).</li> </ol>	<ol style="list-style-type: none"> <li>Detailed calculation of all mineralogical evolutions (dissolutions, precipitations) among clay phases and accessory minerals (hematite, pyrite, calcite, siderite).</li> </ol>	<ol style="list-style-type: none"> <li>/Montes et al. 2005a,b,c,d/. Applied Geochemistry 20, 409–422. Applied Clay Science, 29, 155–171. J. of Environ. Management, 77, 35–46. Applied Clay Science, 30, 181–198.</li> </ol>

Study – Basic information	Materials used	Experimental conditions	Results/Analyses	Documentation
4. 2002–2005.	4. Fe <sup>2+</sup> diffusing in the interstitial fluid of the bentonite from the corroded steel overpack.	4. Up to 150°C (most of the calculations were done at 100°C).	4. Detailed calculation of the composition (Eh, pH, solutes) and activities of ions.	
5. Simulation of the possible feedback effects of geochemical reactions on the transport properties (porosity and diffusion) of a compacted bentonite, up to 100°C, under the influence of the fluids from the surrounding Callovo–Oxfordian geological levels and from the corrosion of the steel overpack.	5. On one side of the simulated barrier the fluid results from the steel overpack corrosion, on the other side from the geological environment.	5. Recalculated by the model at any time and in each bentonite cell (5x5x5 cm): - between 6.2 in the clay phase to about 8. in the vicinity of the source of Fe(II) and up to more than 10. in the corrosion zone.	5. Volumes of minerals in the barrier, porosity, calculated permeability, detailed composition of the aqueous phase in each cell as a function of time.	
6. 2007–2010 – new project to be submitted.		6. Reduced conditions (controlled by H <sub>2</sub> partial pressure).	6. After 100 000 years of simulated mass transport-reaction, the model predicts mineralogical modifications of the barrier in contact with the geological interacting fluid, and with Fe <sup>2+</sup> ions provided by the corrosion of the steel overpack: transformation of the initial montmorillonite by partial illitization, saponification and vermiculitization due to chemical diffusion from geological groundwater through the bentonite barrier. The predicted evolutions of porosity display decreasing values and are limited to the outer parts of the barrier.	

Study – Basic information	Materials used	Experimental conditions	Results/Analyses	Documentation
<p>7. Participation to the ANDRA<sup>®</sup> Verres – Fer – Argiles<sup>®</sup> project (Glass – Iron – Clays) – 2007–2010 : modelling fluid –clays interactions on short term (comparing with experiments conducted by research teams in Nancy) and on long term (about 100 000 years).</p>		<p>7. Simulated storage conditions : coupled transport and reaction.</p>		
<p>8. (1) Thermokinetic model KINDIS (using solid solutions as an option for complex mineral phases like clays).  (2) Coupled transport – reaction model KIRMAT (1D) extended from the KINDIS code.</p>		<p>8. Up to 100 000 simulated years.</p>		<p>/Gerard et al. 1998/ Journ. of Contaminant Hydrology, vol 30/3-4, pp.199–214.</p>
<p>9. Development of the new geochemical code NANOKIN combining kinetic laws for nucleation and growth or dissolution of particles with simulation of Crystal Size Distribution.</p>				<p>/Noguera et al. 2006ab/ J. of Crystal Growth, 297, 180–186.  J. of Crystal Growth, 297, 187–198.</p>