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EFFECTS OF TEMPERATURE, pH, AND IRON/CLAY AND LIQUID/CLAY RATIOS ON EXPERIMENTAL CONVERSION OF DIOCTAHEDRAL SMECTITE TO BERTHIERINE, CHLORITE, VERMICULITE, OR SAPONITE

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Abstract—In deep geological repositories for high-level nuclear wastes, interactions between steel canisters and clay-rich materials may lead to mineralogical transformations with a loss of the confining properties of the clays. Experiments simulating the conversion of smectite to Fe-rich clay phases in contact with Fe metal have been carried out to evaluate such a possibility by taking into account the effects of a series of critical parameters, including temperature, pH, and Fe/clay (Fe/C) and liquid/clay (L/C) ratios. The mineralogical and chemical transformations observed in these experiments have been compared with data from the literature, and subsequently used to propose a conceptual model for the main mineralogical transformations which can be expected in clay formations surrounding high-level nuclear waste repositories. In the presence of Fe metal and under low oxygen fugacity ($<10^{-40}$) the main mineralogical sequences are as follows:

(1) up to 150ºC, under neutral pH, and L/C > 5: dioctahedral smectite (di-sm) → 7 Å Fe-rich phase (berthierine, odinite−cronstedtite) for large Fe/C ratios (>0.5), or di-sm → Fe-rich di-sm + Fe-rich trioctahedral smectite (tri-sm) for small Fe/C ratios (0.1);

(2) up to 150ºC, under alkaline pH (10−12), and L/C > 5: di-sm → Fe di-sm (±palygorskite) for a small Fe/C ratio (0.1);

(3) at 300ºC, Fe/C = 0.1, and L/C > 5: di-sm → Fe-rich saponite → trioctahedral chlorite + feldspar + zeolite (near-neutral pH); di-sm → Fe-rich vermiculite + mordenite (pH 10−12).

Low temperatures (<150ºC) and large L/C and Fe/C ratios seem to favor the crystallization of the serpentine group minerals instead of Fe-rich trioctahedral smectites or chlorites, the latter being favored by higher temperatures. The role of L/C and Fe/C ratios and the competition between them at different temperatures is a crucial point in understanding the transformation of smectite in contact with Fe metal.

Key Words—Berthierine, Chlorite, Fe Metal, Nuclear Waste, Saponite, Smectite, Vermiculite.

INTRODUCTION

The interaction between smectites and Fe metal has been investigated in recent years in response to queries by nuclear-waste management agencies about the long-term behavior of engineered barriers after closure of the repository. Previous works, dealing with Fe-clay interaction, report the formation of distinct types of clays (serpentine-like phases, dioctahedral or trioctahedral Fe-rich smectites, chlorite) and distinct mineral sequences, and sometimes appear to be contradictory. The contradiction has encouraged this comparison of previous experimental conditions and results with new data. In close contact with the waste packages ('near-field system') and in reduced conditions, water is unstable, Fe is released, and H_2 is produced. The main parameters to be considered in such a system are shown in Figure 1 and a summary of the experimental conditions and experimental results described in the literature is presented in Table 1.

Experimental temperatures

Depending on countries and concepts, the initial temperature of the overpack in the repository will vary between 80ºC and 100ºC. The main problem which arises when conducting experiments on smectites at such temperatures is the difficulty in reaching equilibrium, especially when the L/C ratio is small. In engineered clay-barrier conditions, L/C is ~0.2±0.1, and it depends on the density of the bentonite. To compensate for kinetic effects, one possibility is to increase the temperature by conducting the experiments at greater

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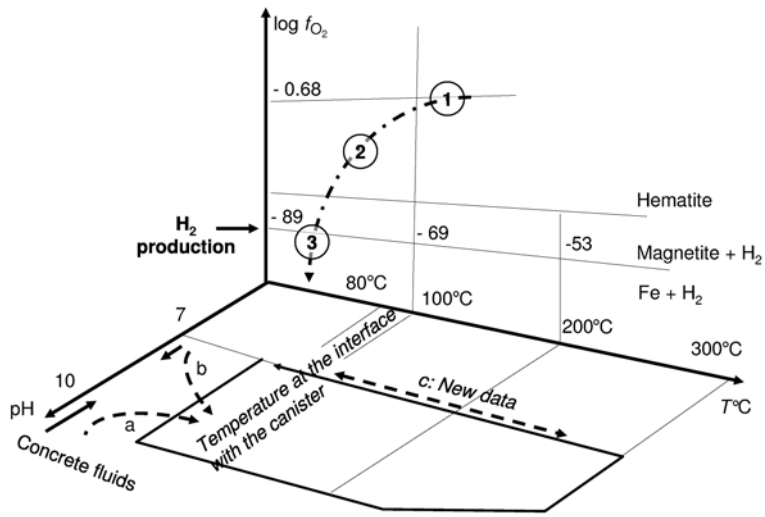


Figure 1. Main parameters taken into account in the experimental modeling of the Fe−clay interactions: (a) pH reduction due to alkaline fluid−bentonite interaction; (b) pH increase due to Fe dissolution; (c) temperature-pH field chosen for new data in this study: (1) excavation under atmospheric f_{O_2}; (2) f_{O_2} reduction while O_2 stock lasts; and (3) instability of water.

temperatures, up to 250−300ºC (Guillaume, 2002; Guillaume *et al.*, 2003, 2004; Wilson *et al.*, 2005, 2006; Charpentier *et al.*, 2006). Another possibility is to increase the reactive surface by increasing the dispersion of particles and the amount of water.

Changes in redox conditions and Fe concentration in the fluids

After closure of the repository, the engineered barrier will be submitted to increasingly reducing conditions (1, 2, and 3 in Figure 1). The scenario includes (1) the consumption of residual oxygen introduced in the pores during the early steps through the oxidation of the Fe^{2+} phases such as pyrite; and (2) the production of H_2 due to the instability of water in the presence of Fe metal (Garrels and Christ, 1965). The Fe metal−water interaction results in a drastic reduction in f_{O_2} to the water instability boundary, *e.g.* within the field of magnetite + H_2, and close to the Fe metal + H_2 field. At an f_{O_2} fixed by the boundary Fe metal/magnetite or less than the f_{O_2} determined by the equilibrium:

$$H_2O \rightarrow H_2 + ½\ O_2$$

the Fe metal is transformed into magnetite following the reaction:

$$3\ Fe^0 + 2\ O_2 \rightarrow Fe_3O_4$$

thus yielding the mass balance reaction:

$$4\ H_2O + 3\ Fe^0 \rightarrow Fe_3O_4 + 4\ H_2$$

Changes in pH and in the ionic strength

The penetration of alkaline fluids issued from the concrete-water interaction in other engineered parts of the repository must result in an increase in pH of the interstitial fluid within the clay barrier. Alkaline fluids are generally progressively neutralized by the interaction with clays, as shown by experiments (trend a in Figure 1). The pH decreases from values of 12 or 10 to ~8.5 (at 80ºC for instance), when no alkaline reserve is introduced, *e.g.* when the alkalinity of the incoming fluid is only considered as a starting experimental feature and is not maintained (Charpentier *et al.*, 2006). The dissolution of Fe metal may produce an increase in pH (trend b in Figure 1) if no other mineral reaction is involved:

$$Fe^0 + 2\ H_2O \rightarrow H_2 + 2\ OH^- + Fe^{2+}$$

When an allochtonous source of fluids is considered, *e.g.* alkaline fluids from the concrete parts of the repository, the ionic strength of the incoming fluids in contact with the steel containers will increase. In such a case, the increasing activity of calcium stabilizes other kinds of minerals such as zeolites (Charpentier *et al.*, 2006).

The reported experiments (Table 1) were carried out in autoclaves in the presence of air, *e.g.* with an O_2 reserve (Lantenois, 2003; Lantenois *et al.*, 2005; Perronnet, 2004; Perronnet *et al.*, 2008), under argon atmosphere (Guillaume *et al.*, 2003, 2004), or under N_2 atmosphere (Wilson *et al.*, 2005). Various amounts of Fe, as powders of metal (Fe^0) and/or oxides (Fe_2O_3, Fe_3O_4), were added to the experimental media leading to different Fe/C ratios, from 0.1 to 2, according to the authors. Liquid/clay ratios also vary. Experiments were conducted at L/C values of 10 (Guillaume *et al.*, 2004; Charpentier *et al.*, 2006), 16.7 (Perronnet, 2004; Perronnet *et al.*, 2008; Lantenois *et al.*, 2005), and

Table 1. List of published results as a function of different physical chemical experimental parameters.

Experiment							Main newly-formed clay phases	By-products	Authors
Mixture	Liquid/clay mass ratio (L/C)	Iron/clay mass ratio (I/C)	Starting redox conditions	Starting pH of experimental solutions	Time	Temperature			
MX80+Fe+magnetite	10 (Na,Ca)-Cl	0.1	Argon atmosphere Fe/magnetite (−550 mV measured)	~7	1−12 months	80ºC and 150ºC	Fe-rich di-sm	Not determined	Guillaume (2002), Guillaume *et al.* (2004)
						300ºC	Fe-rich tri-sm (saponite like) + Fe^{2+}-chlorite	Quartz, feldspar, zeolite (erionite like)	Guillaume *et al.* (2003)
MX80+Fe+magnetite	10 (alkaline solution: $NaCl+Ca(OH)_2$)	0.1	Argon atmosphere Fe/magnetite	12.3	1−9 months	80ºC and 150ºC	di-smectite	Transitory palygorskite	Charpentier *et al.* (2006)
						300ºC	Fe^{2+}-rich vermiculite	Mordenite	Charpentier *et al.* (2006)
Montmorillonite (SWy2)/Beidellite (SBld-1)/Nontronite (Garfield) + Fe (No destabilization of trioctahedral smectites)	16.7 (pure water or spring water)	1 to 2	Atmospheric or argon atmosphere	7 to 11	45 days	80ºC	7 Å phases (gels): Odinite–cronstedtite series	Magnetite	Lantenois *et al.* (2005)
FoCa 7 or Ca-smectite (Prassa) or Ca-nontronite + Fe	16.7 (Evian) or NaCl 15 mmol L^{-1}	0.13 to 0.33	Atmospheric	7.2	1−12 months	80ºC	7 Å phases: berthierine, odinite, cronstedtite (Fe/C = 0.13−0.3 and time = 1−3 months)	Magnetite	Perronnet (2004) Perronnet *et al.* (2008)
Tournemire + Fe					3 months		Not observed		
MX80 + Fe							Not observed		
Purified MX80 + Fe							7 Å phases		
Na-montmorillonite + magnetite + Fe + calcite	66.7 (NaCl solution)	0.57; 0.68; 0.78	<hematite-magnetite N_2 atmosphere	9.73 to 4.15	93, 114 days	250ºC	Fe^{2+} rich smectite (saponite-like)	Magnetite	Wilson *et al.* (2005, 2006)
Na-montmorillonite + Fe	66.7 ($FeCl_2$)	~0.6	>hematite-magnetite	4.24 to 4.71	90, 92 days	80ºC, 150ºC, 250ºC	7 Å phases (berthierine only at 250ºC)		

66.7 (Wilson *et al.*, 2005, 2006). Experiments carried out at high temperature to compensate for kinetic effects yielded to the formation of Fe-saponite and chlorite after dioctahedral Na-Ca smectite at 300ºC (Guillaume *et al.*, 2003) or berthierine-like minerals at 250ºC (Wilson *et al.*, 2005, 2006). At lower temperatures (<150ºC), dioctahedral smectite was sometimes preserved (Guillaume, 2002; Guillaume *et al.*, 2004; Charpentier *et al.*, 2006). On the other hand, Lantenois *et al.* (2005), Perronnet (2004), and Perronnet *et al.* (2008) reported the formation of a 7 Å phase (berthierine or a mineral of the odinite−cronstedtite−greenalite series) for experiments carried out at 80ºC. An overall consideration of the experimental conditions and experimental results compiled from the available data of the literature (Table 1) shows that the mineralogical assemblages obtained after experiment are probably very dependent on parameters such as the Fe/C and the L/C ratios. The purpose of the present study was to evaluate the role of these parameters by comparing published data (Table 1) to results obtained from a new set of experiments carried out at 80ºC, 150ºC, and 300ºC with different Fe/C ratios (0.1 and 0.5) and L/C ratios (5 and 10). The effects of time and temperature, as well as the impact of an increased availability of the Fe metal, were investigated. Special attention was paid to the impact of the distance to the Fe plate on the nature of the run products.

MATERIALS, METHODS, AND ANALYTICAL TECHNIQUES

Batch experiments were conducted at 80, 150, and 300ºC in dilute chlorine solutions (NaCl, $CaCl_2$) having ionic strength and major cation compositions close to the natural waters present in sediments and similar to that of experiments described by Guillaume (2002) and Guillaume *et al.* (2003, 2004). The starting product was a Wyoming bentonite (MX80) consisting of >85 wt.% of smectite. The smectite is a montmorillonite and the half structural formula (<2 μm fraction of the bentonite) given by Guillaume *et al.* (2003) is:

$$(Si_{3.98}Al_{0.02})(Al_{1.55}Mg_{0.28}Fe^{II}_{0.08}Fe^{III}_{0.09})O_{10}(OH)_2Na_{0.18}Ca_{0.10}$$

Bentonite was placed in contact with Fe oxides (magnetite) and Fe metal in autoclaves over periods ranging between 3 and 12 months. The L/C mass ratios were 5 or 10 (rather less than those used in previously published works, see Table 1), and Fe (powder of metal Fe + magnetite)/clay ratios were 0.5 or 0.1. A plate of metallic Fe (~1 cm^2) was added in all experiments. The starting products were introduced into the autoclave under Ar atmosphere. Details of the experimental procedures have been published elsewhere (Guillaume *et al.*, 2003, 2004; Charpentier *et al.*, 2006). The mineralogical and chemical evolutions of the clays were studied by X-ray Diffraction (XRD), Transmission Electron Microscopy (TEM) using High Resolution and Electron Dispersive Spectroscopy (HR- and EDS-TEM), and micro-Fourier Transform Infrared (μFTIR) spectroscopy.

Analysis of particles was coupled with HRTEM images so that particle edges could be observed. X-ray diffraction, carried out on air-dried and glycolated preparations of samples, was used to investigate the swelling feature of the clays and to discriminate the main run products (saponite, vermiculite, and chlorite or berthierine). Serpentine group minerals and Fe-rich chlorite were extremely difficult to distinguish by XRD (because of the similarities of their chemistry and structure − HRTEM was used to help in the identification; and because of the small amount of newly formed phases in comparison to the unmodified starting product). Due to the number of run samples, crystal-chemical trends are presented as they, in particular, show clearly the increasing incorporation of Fe in newly formed phases, the permanence or otherwise of exchangeable cations typical of smectite-type or vermiculite layers, and the changes in the occupancy of the tetrahedral site by Si which was the best indicator of the smectite to non-swelling (chlorite or berthierine) conversion.

The FTIR spectra were obtained in the mid-IR region (4000−600 cm^{-1}) by micro-Fourier Transform Infrared (μFTIR) spectroscopy using a Bruker IFS 55 spectrometer associated with a Bruker A590 microscope. All measurements were conducted in transmission mode on samples deposited on ZnSe slides. The diameter of the beam was 60 μm and the spectral resolution was 2 cm^{-1}. The recording time was ~1 min. Each spectrum was processed using the *OPUS* program (©Bruker).

RESULTS

Effect of Fe/clay ratio

80ºC experiments. At 80ºC for a L/C ratio of 10 and an Fe/C ratio of 0.1, run products were characterized by slight decreases in Si content and interlayer charge (Na + K + 2Ca) together with a slight increase in Fe content (Figure 2). The duration of experiment had no effect on the reaction and a possible equilibrium was obtained after 3 months. In contact with the Fe plate (large Fe/C ratio) and for a short duration (3 months), clay particles were richer in Fe (filled triangles in Figure 2) than the bulk run product.

A more significant evolution was observed for a greater Fe/C ratio (0.5) and for a smaller L/C ratio (5) (gray triangles in Figure 2): these experimental conditions favored the crystallization of an Fe-rich and Si- and Ca-poor phase. The duration of this experiment was important (12 months) but equilibrium was quickly obtained for shorter durations. The XRD patterns showed that the fine fraction (<4 μm) of this last run product (Figure 3) was mostly composed of a swelling clay-like smectite. Additional saturations of this fraction

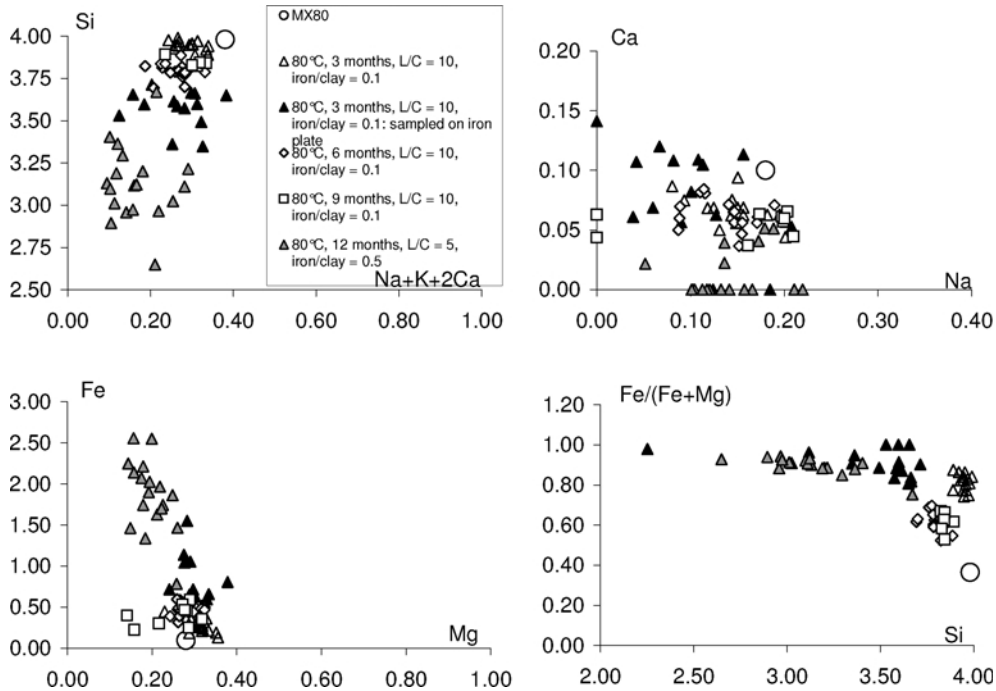


Figure 2. Comparison of the crystal-chemistry of the clay phase for experiments carried out at 80ºC with a L/C ratio of 10 or 5, and an Fe/C ratio of 0.1 or 0.5. The durations were 3 months (open triangles), 6 months (open diamonds), 9 months (open squares), or 12 months (gray triangles). Filled triangles correspond to particles sampled on the Fe plate. The circle corresponds to the range of values of the starting MX80 bentonite Si *vs.* Na + K + 2Ca; Fe (total Fe converted to Fe^{3+}) *vs.* Mg; Ca *vs.* Na; and Fe/(Fe + Mg) *vs.* Si diagrams plotted from EDS-TEM analyses and structural formulae calculated on the basis of 11 oxygens (diagrams after Grauby *et al.*, 1993).

with Li and Mg before XRD analysis confirmed that a significant proportion of the run product was fully expandable. The run product could be thus a mixture of a smectite and an Fe-rich 14 Å chlorite (chamosite type) or a 7 Å clay (berthierine type) since the global interlayer charge of the particles decreases. The disagreement between XRD and EDS-TEM results could be explained by a mechanical enrichment in smectite particles during

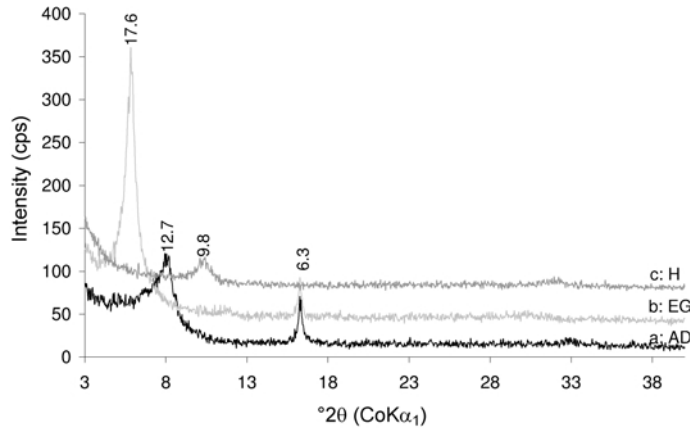


Figure 3. XRD patterns recorded from the fine fraction (<4 μm) of the run product obtained in the 12-month experiment carried out at 80ºC in the presence of a large Fe/C ratio (0.5) and L/C ratio of 5: (a) air-dried sample (AD); (b) glycolated sample (EG: solvation with ethylene glycol vapor at room temperature over 24 h); and (c) heated sample (H: 4 h at 550ºC). The index of reflections corresponds to d_{hkl} in Å. The XRD data were collected using a D8 Bruker diffractometer with CoKα_1 radiation (λ = 1.7902 Å). The general operating conditions were 35 kV accelerating voltage, 45 mA intensity, step-scanning at 0.035º2θ intervals, 3 s counting time, 3−40º2θ for oriented powder.

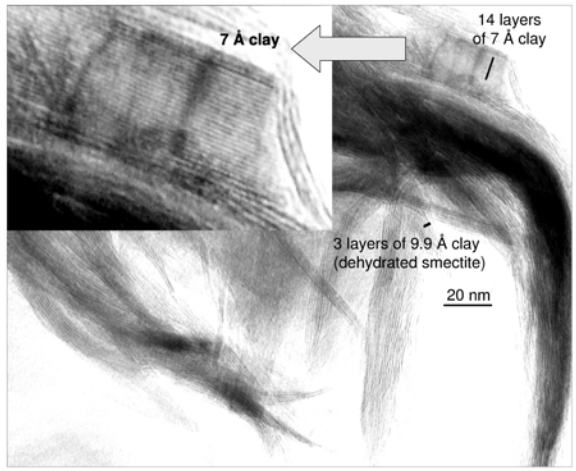


Figure 4. HRTEM analysis of the run product obtained from the 12-month experiment carried out at 80ºC in the presence of a large Fe/C ratio (0.5) and L/C ratio of 5.

the separation of the <4 μm fraction for X-ray analysis. A HRTEM image of the bulk of this run product shows both numerous long flakes typical of smectite (10 Å interlayer) and several shorter and thicker particles with a 7 Å interlayer (Figure 4) and confirmed the coexistence of at least two types of clay in the run sample. The 7 Å Fe-rich phase was, therefore, mostly found for experiments with a large Fe/C ratio. The 7 Å phase had a composition close to that of berthierine (gray triangles in Figure 2) and its abundance decreased to undetectable amounts in experiments carried out with smaller Fe/C ratios. Clay particles of this run product were also sampled at the contact with the Fe plate and analyzed by FTIR spectroscopy. The IR spectrum (Figure 5) was compared to that of the starting Na-montmorillonite (MX80). In the spectra for both the starting montmorillonite and the run product, bands observed between 3800–3100 cm^{-1} and 1700–1500 cm^{-1} were assigned to OH-stretching vibrations from clay minerals and water and to water-bending vibrations, respectively. The spectrum of the run product showed several new bands at 1410, 1385, 1356, 712, and 667 cm^{-1}. By comparison with literature data (Saumagne and Josien, 1962; Toppani *et al.*, 2005), these bands were assigned to stretching (between 1410 and 1356 cm^{-1}) and bending modes (712 and 667 cm^{-1}) of the CO_3^{2-} group. Otherwise, the bending band fitted at 1585 cm^{-1} was assigned to strongly bound water. This kind of FTIR spectrum was very similar to that obtained by Toppani *et al.* (2005) for complex hydrated carbonates. The starting MX80 bentonite containing ~2% carbonates would be the source of CO_2 in the experimental system, allowing the formation of bicarbonates at the contact with the Fe plate.

300ºC experiments. The impact of the Fe/C ratio on the transformation of montmorillonite at three different experiment durations (3, 6, and 9 months) was studied (Figure 6). Experiments with a small Fe/C ratio (0.1, diamonds in Figure 6) and with a large Fe/C ratio of 0.5 (squares) were compared. The EDS-TEM analyses showed that the increase in Fe/C ratio enhanced the chemical evolution. The decrease in Si content was more significant (Si <3 for a half formula based on 11 oxygens) in run products obtained in experiments with an Fe/C ratio of 0.5 for all durations and in the 9 month experiment only when the Fe/C ratio was 0.1. A long experiment (9 months) and a small Fe/C ratio had the same impact on the tetrahedral occupancy as a short experiment (3 months) and a large Fe/C ratio. Different Fe/C ratios also yielded distinct octahedral occupancies

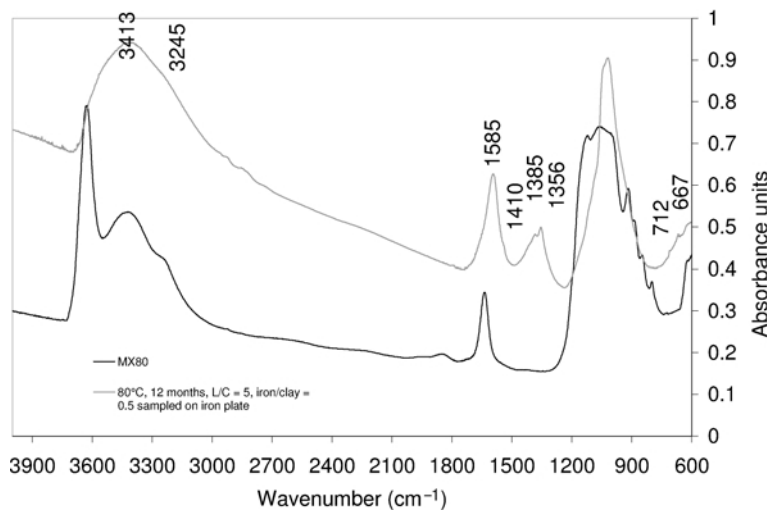


Figure 5. IR spectra in transmission mode of the starting MX montmorillonite and the run product sampled at the contact of the Fe plate in 80ºC, 12 months, L/C = 5, Fe/C = 0.5 experiment.

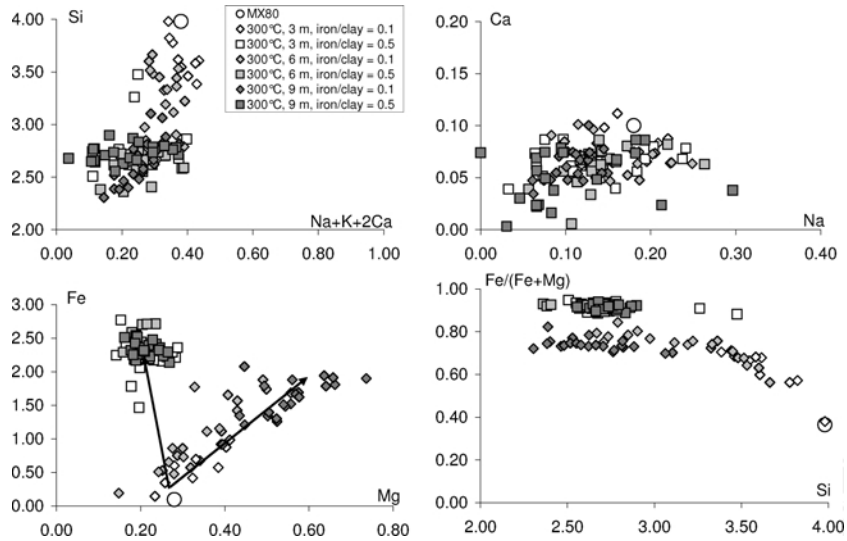


Figure 6. Comparison of the crystal chemistry of the clay phases for 3-, 6-, and 9-month experiments carried out at 300ºC with a L/C ratio of 10, and different Fe/C ratios (0.1 or 0.5). Si *vs.* Na + K + 2Ca; Fe (total Fe converted to Fe^{3+}) *vs.* Mg; Ca *vs.* Na; and Fe/(Fe + Mg) *vs.* Si diagrams are plotted from EDS-TEM analyses and structural formulae calculated on the basis of 11 oxygens (diagrams after Grauby *et al.*, 1993).

of the run clays. In the small Fe/C-ratio (0.1) experiments, both Fe and Mg enrichments were observed in run products (arrows in Figure 6) whereas a large Fe/C ratio in the experimental medium led to a significant Fe enrichment of clays only. Interlayer occupancy of the run products was generally depleted both in Ca and Na for all run products. The new data obtained at 300ºC from greater Fe/C-ratio experiments were in good agreement with results obtained by Guillaume *et al.* (2003) and Charpentier *et al.* (2006) who demonstrated that the chemical evolution of the montmorillonite in MX80 bentonite depends on the distance to the Fe plate and consequently on the availability of Fe in the medium. Iron enrichment in particles sampled near and at the contact with the Fe plate (where the Fe/C ratio was large) was always far more significant.

Effect of temperature

One of the most important parameters controlling the transformation of smectite is temperature. Its effect was also studied in the presence of a metallic Fe plate and under an Fe/C ratio of 0.5 and a L/C ratio of 5. Three long duration experiments (12 months) were conducted at 80ºC, 150ºC, and 300ºC. They showed that the increase in temperature both enhanced Si depletion and Fe enrichment of the run clays (Figure 7). The interlayer charges were different in newly formed clays yielding to the formation of Fe-rich saponite at 300ºC (Na + K + 2Ca ~ 0.3 to 0.4) and the crystallization of a 7 Å phase mixed with starting smectite at a temperature of <150ºC (Na + K + 2Ca <0.2). In the greater Fe/C-ratio (0.5) experiments, no zeolite by-products were observed, regardless of the temperature.

DISCUSSION AND CONCLUSIONS

Mineralogical transformations and sequences

From literature data (Table 1) and results presented in the present paper, at 80ºC and 150ºC, in the presence of Fe (powder and plate) and Fe oxides (magnetite), and for specific experimental conditions (large L/C ratio and Fe/C <0.5), montmorillonite evidently remains the predominant clay mineral in run products. Under any pH (neutral or alkaline), similar weak enrichment of Fe and depletion of Si were observed in the clays. At 300ºC, vermiculite was predominant, associated with Fe-rich trioctahedral smectite (saponite-type) in alkaline conditions (Charpentier *et al.*, 2006) whereas Fe-rich chlorites associated with Fe-rich trioctahedral smectite (saponite-type) were identified in neutral conditions (Guillaume *et al.*, 2003, 2004). The experimental crystallization of Mg-vermiculite after smectite in alkaline solutions was also mentioned by Chermak (1992). In the study of Charpentier *et al.* (2006), the formation of Fe-rich vermiculites seemed to be favored by the initially alkaline conditions and the presence of Fe metal, all other conditions being equal in comparison with the 300ºC experiments reported by Guillaume *et al.* (2003). In all cases, chemical zoning was observed from the very near contact with the Fe plate toward the bulk clay, usually a decrease in Fe in the run products sometimes in favor of Mg (at 300ºC).

The occurrence of quartz, feldspars, magnetite, and zeolites as reaction by-products in all experiments is consistent both with thermodynamic modeling predictions (Cathelineau *et al.*, 2001; Kluska *et al.*, 2002; Montes *et al.*, 2005) and data from other experiments on bentonites (Table 1). The simplified conversion of a

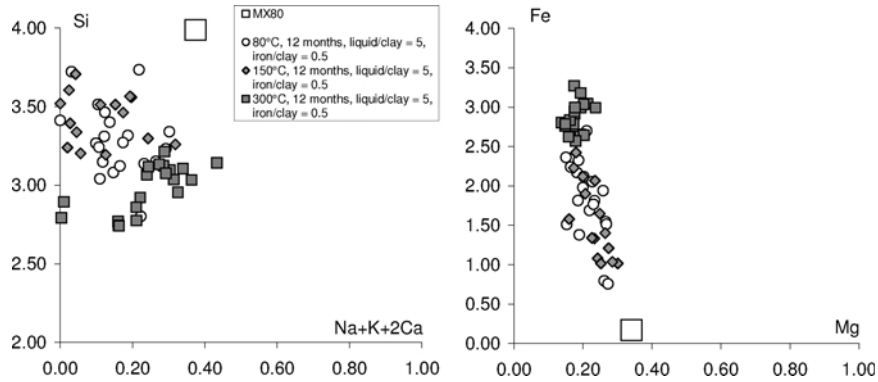


Figure 7. Comparison of the crystal chemistry of clay particles obtained from the 12-month experiments carried out at 80ºC (open circles), 150ºC (gray diamonds), and 300ºC (gray squares) in the presence of an Fe/C ratio of 0.5 and an L/C ratio of 5.

montmorillonite to a chlorite of chamosite-type $(Si_3Al)(Al)(Fe^{2+},Mg)_5O_{10}(OH)_8$ (or berthierine which has nearly the same chemical formulae based on 5 oxygens) yields to the expulsion of silica, which crystallizes either as quartz or other silicates (feldspars, zeolites) depending on the availability of cations in solution. For the material studied, it can be expressed as follows:

$$2\,(Si_{3.98}Al_{0.02})(Al_{1.55}Mg_{0.28}Fe^{II}_{0.08}Fe^{III}_{0.09})O_{10}(OH)_2Na_{0.18}Ca_{0.10} + \text{Montmorillonite MX80 (Sm)}$$
$$7.039\ Fe^{2+} + 10.76\ H_2O + 0.18\ e^- \rightarrow$$
$$1.57\,(Si_3Al)(Al)(Fe^{II}_{4.7}Mg_{0.3})O_{10}(OH)_8 + \text{Chamosite or 3.14 berthierine (chl)}$$
$$0.2\ Ca^{2+} + 0.36\ Na^+ + 3.25\ SiO_{2\,(aq.)} + 0.089\ Mg^{2+} + 12.96\ H^+ \quad (1)$$

As the dissolution of Fe metal is expressed as:

$$Fe^0 + 2\ H_2O \rightarrow H_2 + 2\ OH^- + Fe^{2+} \quad (2)$$

and reduction of Fe^{3+} to Fe^{2+} is expressed as:

$$Fe^{3+} + \tfrac{1}{2}H_2 \rightarrow Fe^{2+} + H^+ \quad (3)$$

the combination of reactions 1, 2, and 3 results in:

$$7.039\ Fe^0 + 11.698\ H_2O + 2\ Sm \rightarrow 1.57\ Chl + 0.2\ Ca^{2+} + 0.36\ Na^+ + 3.25\ SiO_{2\,(aq.)} + 0.089\ Mg^{2+} + 6.949\ H_2 + 0.938\ OH^-$$

The production of H^+ in reaction 1 partly compensates the production of OH^- due to the dissolution of Fe (reaction 2), thus explaining the near-neutral pH of most experimental solutions (measured after quenching). The availability of silica and cations in solution led to the formation of feldspars or zeolites. The presence of bicarbonates or carbonates at the contact of the Fe plate in one experiment is analogous to corrosion products of the steel canister reported in the literature (*e.g.* Schlegel *et al.*, 2008) and the results of geochemical modeling of Fe-clay interactions (Bildstein *et al.*, 2006; Savage *et al.*, 2010). Discrete calcite originally present in the bentonite probably dissolved at the beginning of the experiment. The Ca^{2+} ions released can enter the interlayer space of smectite and HCO_3^- can combine with other cations as Fe^{2+} at the contact of the Fe plate to form hydroxy-carbonate (or carbonate) species. Neutral to high pH values at the contact with the Fe plate (as shown by the presence of magnetite in some experiments) and a small P_{CO_2} could favor the formation of hydroxycarbonates.

Finally, the mineralogical sequences depend on the availability of Fe in solution and on the starting pH of the solution. Under neutral pH conditions, the sequence of newly formed mineral assemblages is thus as follows:

(1) dioctahedral smectite (di-Sm) > Fe-rich di-Sm for small Fe/C ratios and small L/C ratios, or berthierine-like mineral if the Fe/C ratio is >0.5 at 80ºC or 150ºC;

(2) di-Sm > Fe di-Sm > Fe-saponite > trioctahedral chlorite + feldpars + zeolite, at 300ºC.

Experiments carried out with a starting pH of 12 led to the following mineral sequences:

(1) di-Sm > Fe di-Sm + palygorskite at 80º and 150ºC,

(2) di-Sm > vermiculite (± Fe saponite) + mordenite at 300ºC

The possible mineral zonings are, therefore, distinct when the fluids come from the geological barrier or from concrete.

Comparison with natural occurrences

An additional line of comparison is provided by the consideration of natural assemblages and the following transitions: the berthierine-to-chlorite conversion (Iijima and Matsumoto, 1982; Hillier and Velde, 1992), the di- to trioctahedral smectite transition (Inoue, 1987; Inoue and Utada, 1991), and the smectite-to-chlorite conversion (Bettison-Varga and Mackinnon, 1997; Robinson *et al.*, 2002; Schiffman and Staudigel, 1995). The temperature range of stability of chlorite is rather large, between 110ºC and 420ºC (Iijima and Matsumoto, 1982; Cathelineau and Izquierdo, 1988; Hillier and Velde, 1992; Buatier *et al.*, 1993; Aagaard *et al.*, 2000) indicating a potential formation of chlorite minerals at temperatures close to those of interest in waste disposal.

The coexistence of dioctahedral smectite and chlorite is frequent above 160ºC in geothermal systems where minerals are directly precipitated from a fluid and do not derive from the alteration of a clay precursor (Cathelineau and Nieva, 1985; Cathelineau and Izquierdo, 1988; Bailey, 1994). Fe-rich chlorites have also been described in sandstone reservoirs at temperatures of 100−120ºC. Berthierine has been observed mostly in sedimentary basins as an early, low-temperature diagenetic phase (15−40ºC), of which the upper limit of stability is within the 65−130ºC temperature range (Iijima and Matsumoto, 1982; Aagard *et al.*, 2000). Above 160ºC, berthierine is entirely converted to chamosite in natural systems through mixed layering (Hillier and Velde, 1992), and, experimentally, above 200−250ºC (Aagard *et al.*, 2000). Ca-zeolites (laumontite, clinoptilolite, mordenite) are commonly observed associated with smectite and chlorite as alteration products of basic glasses of magmatic rocks submitted to hydrothermal alteration (Cathelineau and Nieva, 1985; Alt *et al.*, 1986; Schiffman and Fridleifsson, 1991, among others). For diagenetic settings, Gündogdu *et al.* (1996) suggested that the formation of zeolites and the amount of zeolites being formed could also be controlled by the amount of Fe released during the dissolution of volcanic glass. Those authors showed that a large Fe content favors the formation of smectite rather than zeolite (especially clinoptilolite). The experiments carried out at various Fe/C ratios (Table 1) confirm this suggestion. At 300ºC, zeolites are only observed for experiments with small Fe contents (Fe/C = 0.1) (Guillaume, 2002; Guillaume *et al.*, 2004; Charpentier *et al.*, 2006). In lower-temperature experiments (80ºC or 150ºC), zeolites do not form probably because of kinetic effects (Guillaume, 2002; Guillaume *et al.*, 2004; Perronnet, 2004; Charpentier *et al.*, 2006, Perronnet *et al.*, 2008). At the same low temperatures but in experiments with large Fe contents (at the contact with the Fe plate and for Fe/C ratios > 0.5), zeolites were not observed.

The experimental mineral assemblages observed in the present experiments and in experiments described in the literature are, therefore, compatible with those found in nature as the upper boundary of berthierine is at ~120−130ºC and the lowest temperature estimated for chlorite is ~110ºC. Authigenic dioctahedral smectite and chlorite are found in the same samples as co-existing phases, possibly at equilibrium, among a large range of temperature from 160 to 240ºC, while saponites are mostly found in the presence of fluids having a greater ionic strength (close to or above sea water) than hydrothermal waters from geothermal systems related to volcanic activity.

Redox conditions and role of intermediate f_{O_2}

The overall consideration of the experimental sets of data indicates that the redox state of the system and the availability of Fe seem to be the two main critical parameters which control the formation of the Fe-rich mineral phases and their relative abundance. In fact, the main changes in physical-chemical parameters concern the redox conditions which dramatically reduce toward the f_{O_2} close to water dissociation, and the production of H_2, which has been confirmed experimentally in some Japanese experiments which show the bubbling of H_2 at the Fe/C interface (Idemitsu *et al.*, 2002). The subsequent increase in pH due to Fe dissolution is balanced by smectite-to-berthierine or chlorite conversion.

The above-mentioned sequences are distinct from that proposed for greater f_{O_2}, lower temperatures (<150ºC), and very large L/C ratios where the predominant newly formed phases are serpentine-group minerals (odinite−cronstedtite, Lantenois, 2003; Lantenois *et al.*, 2005; Perronnet, 2004; Perronnet *et al.*, 2008). The discrepancy is mostly linked to the role of: (1) the L/C ratio: when <5, the fluid chemistry is buffered by the smectite and its evolution toward 7 Å phases seems either impossible or very slow; (2) the redox conditions: under intermediate f_{O_2}, Fe^{2+}/Fe^{3+} phases of the serpentine group are favored, while under the conditions of water instability, Fe-rich dioctahedral or trioctahedral smectite forms at low temperatures (<150ºC), and chlorite or vermiculite form at temperatures above 200−250ºC. A schematic impression of mineral zoning taking into account the redox state, the availability of Fe, and the L/C ratio at low temperatures (<150ºC) is presented in Figure 8.

The nature of the non-swelling Fe-rich clay (7 Å *vs.* 14 Å phases) is debatable mostly because of the difficulty in determining the exact structure of a phase which is limited in quantity, and mixed mechanically or structurally (mixed-layering) with other minerals such as di- or trioctahedral smectites. A considerable set of arguments exists in favor of the formation of chlorite at high temperature and this mineral is also predicted by geochemical modeling of the smectite-Fe interaction, even at 80ºC (Kluska *et al.*, 2002; Montes *et al.*, 2005). Alternately, a series of smectite-Fe experiments resulted in the formation of a 7 Å phase at lower temperatures (80ºC, 150ºC) when the Fe/C and L/C ratios are large. Their stability field seems to have been increased by more oxidizing redox conditions, which favor serpentine-group minerals. The two groups of minerals, chlorite and Fe-serpentine, can thus be formed, but the exact time-temperature pairs delimiting their formation remains poorly known. New data presented here show that for 1 y experiments, the temperature boundary could be between 150 and 300ºC, but these data cannot be extrapolated to other time-temperature pairs close to those of interest for waste disposal (e.g. 1000 to 10,000 y/ 50−80ºC for instance).

Role of the smectite-Fe contact on the smectite conversion rate

A role of the direct contact between Fe metal and clay has been put forward by Perronnet (2004) as a necessary

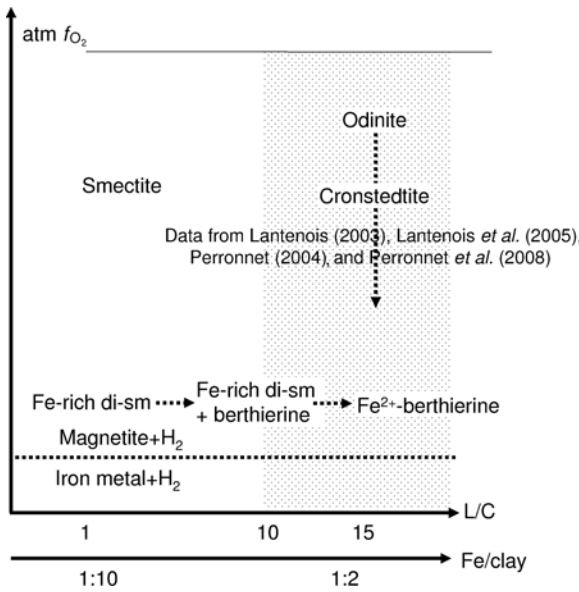


Figure 8. Schematic impression of mineral zoning taking into account the redox state, the availability of Fe and the L/C ratio at low temperature (<150ºC).

condition for the smectite–berthierine conversion. The results of the present study show, however, that 7 Å or 14 Å phases may form at distinct distances from the Fe plate, but with distinct Fe contents. The clay minerals crystallized at more than a few mm from the Fe plate are Mg-rich whatever their nature (chlorite or vermiculite). In any case, the rate of alteration of the clay barrier will be extremely dependent on the ability of Fe to migrate through the clay barrier as Fe^{2+}. This process is controlled by: (1) the rate of corrosion of iron; (2) the rate of formation of a possible crust of magnetite (or siderite when P_{CO_2} is increased) at the interface with the Fe canister, which may reduce the amount of Fe^{2+} released to the system; and (3) the dynamics of migration of Fe through diffusion processes.

Consequences for swelling properties

The transformation of montmorillonite into the association of serpentine-like or chlorite phases might lead to significant modifications of the material properties (Devineau *et al.*, 2005). On the contrary, the formation of saponite or vermiculite, *e.g.* minerals having swelling properties has a less critical effect on the swelling properties of the bentonite, than the formation of chlorite or a serpentine-like phase. The vermiculitization of montmorillonite is accompanied by a reduction of the structural Fe in the newly formed clay particles. The reduction in Fe may influence the properties of smectite (Stucki and Tessier, 1991; Stucki *et al.*, 1984a, 1984b; Lear and Stucki, 1989). Lear and Stucki (1989) described, for example, the decrease in swelling capacity and of the specific surfaces of nontronite due to the collapse of some interlayers after Fe reduction. In addition, the proportion of swelling phases decreases as some of the material is converted to a non-swelling phase (zeolite). Besides, zeolites such as mordenite have a large cation exchange capacity and large adsorption capacity (Pabalan, 1994). The exchange and adsorption capacities of the zeolite + vermiculite assemblage may be thus as important as those of the initial bentonite.

Extrapolation of results to small-water-content bentonite and low temperatures

With regard to a nuclear waste repository, the experimental simulations above have demonstrated an evolution toward clay minerals with smaller CEC values. The transformation was observed to its greatest extent nearest to the contact with the added metallic Fe plate and under specific experimental conditions favoring the reactions. Prediction of the potential behavior of smectite in the presence of a steel container and their related alteration products, under nuclear-waste-repository conditions, is made difficult by the likely temperature range of 25−90ºC. Under such low temperatures, very little mineralogical change could be determined from experiments carried out over short durations (<1−2 y) and for liquid/mineral ratios typical of an engineered barrier (<0.1). Experiments carried out at higher temperatures could, however, be extrapolated to lower temperatures as the type of mineralogical changes observed at high temperature is predicted by numerical modeling either at high (300ºC) or much lower temperatures (80−100ºC). However, kinetic predictions using constraints from temperature-time pairs still require experimental calibration.

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