

## Evidence of a critical content in Fe(0) on FoCa7 bentonite reactivity at 80 °C

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### Abstract

In order to assess the evolution of the confinement properties of clay engineered barriers (EBS) when in contact with metallic canisters containing radioactive wastes, Fe(0)-bentonite interactions need to be assessed. “45 days–80 °C” tests were performed using powdered FoCa7 bentonite and metallic iron. Since one fundamental parameter may be the available quantity of Fe(0), a wide range of Iron/Clay mass ratios (I/C) from 0 to 1/3 is used. The confinement power of clay material results from the swelling properties and the retention capacity. Thus, the major criterion which is chosen to assess the evolution of the confinement properties in this study is the variation of Cation Exchange Capacity (CEC). In parallel, the physico-chemical evolution of bentonite is studied using XRD and EDS-TEM microanalyses. The evolution of the distribution of iron environments is obtained by <sup>57</sup>Fe Mössbauer spectroscopy.

This study evidences that both kaolinite and smectite from the bentonite are altered into SiAlFe gels when in contact with Fe(0). These gels maturates into Fe-rich di-trioctahedral phyllosilicates, whose composition is bounded by the one of odinite and greenalite in a Fe–M<sup>+</sup>–4Si diagram when I/C=1/3. Most of all, it is evidenced that the reaction depends on the available quantity of Fe(0). When the I/C ratio is between 1/30 and 1/7.5, the exchange capacity of FoCa7 bentonite starts decreasing, the consumption of Fe(0) becomes significant, the alteration of smectites occurs and secondary oxides are formed. The crystallization of Fe-rich phyllosilicates is observable when I/C ratio is higher, from a threshold between 1/7.5 and 1/5. Above I/C=1/3.75, initial iron oxides are strongly consumed and participate in the incorporation of Fe<sup>2+</sup> and Fe<sup>3+</sup> in gels or new phyllosilicates octahedra.

These experimental results were used as input data for the prediction of the long-term evolution of the EBS using Crunch reaction-transport model.

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**Keywords:** Bentonite; Smectite; Metallic iron; Iron–clay mass ratio; CEC; 7 Å Fe-rich clays

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## 1. Introduction

Some designed concepts for the disposal of high level radioactive wastes (HLW) in deep geological formations envisage the use of a clay engineered barrier system (EBS) (Andra, 2005a,b). Clay material is of a great interest for geo-containment because of its low hydraulic conductivity, plastic and sealing properties and high sorption and swelling capacities. Repositories may include high amounts of metallic iron, mainly used as containers but also as supporting structures. Interactions between clay materials and Fe(0) are to be expected. The metallic components will undergo a corrosion process by oxygen and then by groundwaters. In several HLW projects, the expected maximal temperature is below 100 °C and after an oxidizing stage, due to construction works, the system will progressively become reduced, illustrating the redox buffer effect of the deep host-rock. The initial characteristics of the clay material will certainly evolve during disposal lifetime, which is of concern for assessing the long-term evolution of the confinement of radionuclides in the facility. Consequently, as part of the near field research program, experiments are performed to assess the clay stability and the potential changes in their physico-chemical properties when in contact with metallic iron for different temperatures, saturation states and redox conditions.

Some potential natural analogues describing the iron–clay reactivity are found in soils and in sedimentary and diagenetic processes. In soils, oxidation–reduction reactions are one of the mechanisms which control the evolution of clay minerals. For example, in samples coming from rice field soils, drastic variations in Cation Exchange Capacity (CEC) were observed as the consequences of the formation of Fe-rich chlorites or 1:1 minerals (Favre et al., 2002). Low temperature, iron-rich, argillaceous environments are also described in

sedimentary verdine facies (Bailey, 1988; Odin, 1988, 1990), in diagenetic oolitic ironstones (Bhattacharya, 1983, 1986) and in sandstones (Hillier and Velde, 1992; Hillier, 1994; Hornibrook and Longstaffe, 1996; Aagaard et al., 2000). In oxidant marine environments, at about 20°C, green clays, such as glauconite or odinite, are observed (Odin, 1988). Glauconite results from the dissolution–crystallization of Fe-rich smectite (Buatier et al., 1989) and odinite occurs in shallow marine shelves and reef lagoonal areas under tropical latitudes, in local anoxic to reducing microsystems (Odin, 1988). In these systems, redox fronts occur and ferric iron oxo-hydroxides are reduced. Through this process, ferrous iron is released and reacts with colloids and smectites gels to allow the crystallization of odinite. Deeper, as temperature increases and the medium becomes reducing, the 7 Å phases can evolve into Fe-rich chlorite, via 7 Å/14 Å mixed layers, as inferred by observations at 70 °C by Hornibrook and Longstaffe (1996) or at 195 °C by Walker and Thompson (1990).

The transposition of such analogues to waste disposal systems is somewhat limited since they contain no metallic iron reacting with clays unlike in HLW repositories. But some Fe(0)/clays interactions are identified in the low temperature aqueous alteration of meteorites, early in their history (Zolensky and McSween, 1988). This phenomenon is described in the case of carbonaceous chondrites, such as CMs, and occurs on the parent-bodies when heating of the asteroid induces fusion of accreted ice (Zolensky and McSween, 1988; Brearley, 1997; Zega and Buseck, 2003). The estimated temperature at which alteration takes place is low, between 20 and 150 °C, and differs from one meteorite to another (Zolensky and McSween, 1988; Brearley and Jones, 1998). In these systems, the fluid/rock ratio is low to moderate (Zolensky and McSween, 1988) and the pressure can be considered to be negligible because of the very small size of asteroid. CM carbonaceous

Table 1  
Previous experiments conducted on the iron–clay reactivity

Clay	Iron supply	Aqueous solution	T (°C)	Duration (months)	I/C	C/S	References
Purified smectites	Fe(0)	Distilled water	80	1.5	2	1/16.7	Lantenois, 2003, Lantenois et al., 2005
Smectite MX80	Fe(0)	CaCl <sub>2</sub> MgCl <sub>2</sub>	200	1 and 2	1/30	1/16.7	Habert (2000)
	Mt+Hm	NaCl+CaCl <sub>2</sub>	80	3 and 9	1/10	1/10	Guillaume et al. (2003)
	Mt+Hm		300	1, 3 and 9			
	Fe(0)+Mt		300	3 and 9			
FoCa7	Fe(0)+Mt+Pl		300	1, 3 and 9			
	Steel plate	Granitic water	80	8	/	1/0.4	Papillon et al. (2003)
FoCa7	Steel cylinder	Granitic groundwater	170 max	6 and 48	/	1/0.3	Latrille et al. (2001)
FoCa7	Fe(0)	Evian	80	1.5	0 to 1/3	1/16.7	This study

Fe(0): Fe(0) powder, Mt: magnetite, Hm: hematite, Pl: iron plate, I/C: iron–clay mass ratio, C/S: clay–solution mass ratio.

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