

Long-term (8-10 y) alteration of bentonite in the presence of metallic iron

S. Kumpulainen¹, T. Carlsson², A. Muurinen², D. Svensson³, H. Sasamoto⁴, M. Yui⁴, P. Wersin⁵ & M. Snellman⁶

1. B+Tech Oy, Laulukuja 4, 00420 Helsinki, Finland (sirpa.kumpulainen@btech.fi)
2. Technical Research Centre of Finland (VTT), P.O.Box 1000, 02044 VTT, Finland (torbjorn.carlsson@vtt.fi, arto.muurinen@vtt.fi)
3. Swedish Nuclear Fuel and Waste Management Co (SKB), P.O.Box 300, 57295 Figeholm, Sweden (daniel.svensson@skb.se)
4. Japan Atomic Energy Agency (JAEA), Geological Research and Development Directorate, Muramatsu, Tokai-Mura, Naka-guu, Ibaraki, 319-1194, Japan (sasamoto.hiroshi@jaea.go.jp, yui.mikazu@jaea.go.jp)
5. Gruner Ltd., 4020 Basel, Switzerland (paul.wersin@gruner.ch)
6. Saanio&Riekkola Oy, Laulukuja 4, 00420 Helsinki, Finland (margit.snellman@sroy.fi)

Posiva and SKB are developing a horizontal nuclear waste repository design alternative (KBS-3H) (SKB/Posiva 2008). Similar design has also been considered in Japan as PEM (Prefabricated EBS Module) with iron canister (NUMO, 2004). In the KBS-3H design, each canister, with a surrounding layer of bentonite clay, is placed in a perforated steel cylinder prior to disposal underground; the entire assembly is called the supercontainer. Several supercontainers are positioned along up to 300 m long deposition drifts, which are sealed following canister emplacement using drift end plugs. The carbon steel shell is expected to corrode at the repository conditions. Interactions with dissolved Fe, hydrogen gas and other reaction products may lead to the alteration of the bentonite buffer and thus impair its safety functions. Thus, it is essential to get a better understanding of long-term alteration processes of bentonite in contact with iron.

Materials and Methods

Two set of samples were studied: 1) MX-80 bentonite samples, which were compacted around one cast Fe cylinder and were in contact with 0.5 M NaCl salt solutions for 8 y, and 2) 10 y old batch tests with Kunipia-F purified bentonite and fine iron powder, which were in contact with deionized water, 0.3 - 0.6 M NaCl, 0.1 M NaHCO₃ or 0.05 M Na₂SO₄ salt solutions. The compacted Fe-bentonite test setup is considered to represent conditions resembling those of a nuclear waste repository, whereas batch tests are considered to represent extreme situations due to their much higher iron to smectite ratio (1/1). Both set of samples were kept in N₂-atmosphere (< 1 ppm) and room temperature for 8 - 10 y. Chemical compositions of gas, external solution, and bentonite solid were analyzed with GC, IC, FAAS, ICP and SEM-EDS. Eh and pH were determined both of external solutions as well of porewater inside the compacted bentonite. The bentonite solid material was characterized with exchangeable cation extractions, CEC, FTIR, XRD, XANES, TEM and Mössbauer spectroscopy. In addition, physical properties (density, swelling pressure, hydraulic conductivity) were determined.

Results

8 y old compacted bentonite samples:

The gas phase contained rather elevated concentrations of H₂ (caused by the corrosion of the cast iron cylinders) and of CO₂ (as a result of calcite dissolution), but no detectable amounts of O₂. The external solutions showed increased alkalinity, Mg, Ca, and SO₄ concentrations, and decreased concentrations of Na and Cl. Preliminary results indicate that pore water pH was 7.9 - 8.2 and that Eh, when measured with a Pt electrode, was in the range -210 to -488 mV. In bentonite, a brown iron diffusion front in bentonite extending to 7 - 8 mm distance from cast iron was observed. The results indicate a slight increase in CEC (from 950 to 990 meq/kg) and a significant increase in exchangeable iron (from 0 to 10 meq/kg) and in total Fe content (from 4 to 15 wt %) towards the cast iron source (Figure 1). In

addition, a decrease in total Si content of bentonite towards cast iron was observed. In the close vicinity of cast Fe, the precipitation of aragonite was observed. FTIR analyses suggested that the transferred iron is incorporated to some extent in the montmorillonite structure. A decrease in swelling pressure but no change in hydraulic conductivity was observed in undisturbed samples. However, after drying, mixing and recompaction no clear differences between reference sample and Fe-reacted sample with regard to swelling pressure and hydraulic conductivity were found. The initial decrease in swelling pressure, the rigid behavior of Fe-bentonite samples observed during dismantling, as well as in SEM analysis suggested that bentonite had been cemented to some extent due to interaction with cast iron. These observations are consistent with earlier work of Carlson et al. (2007) and Milodowski et al. (2009).

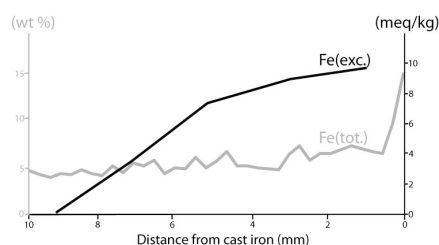


Figure 1. Semiquantitative total Fe content and exchangeable Fe content of MX-80 bentonite as a function of distance from cast iron.

10 y old batch samples:

All 10 y old batch samples had high pH-values (pH 11.1 - 12.8) and exhibited strongly reducing conditions (Eh(Pt) -446 - -611 mV). Montmorillonite had transformed to a non-swelling 7 Å clay mineral in samples stored in 0.3-0.6 M chloride solutions and in 0.1 M bicarbonate solution. Based on XRD (Figure 2) and FTIR determinations, the 7 Å non-swelling clay phase formed is serpentine mineral (berthierine). Samples exposed to distilled water and 0.05 M sulphate solutions did not show any smectite alteration and contained, in addition to montmorillonite, magnetite or pyrite, respectively. The results suggested that the transformation of montmorillonite was affected by the pH increase caused by metallic iron corrosion, formation of corrosion products (e.g. magnetite) and the amount of ferrous iron in the system.

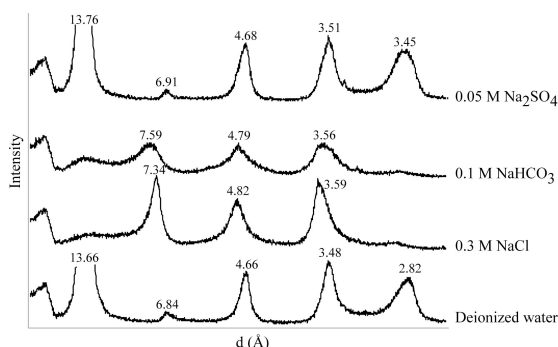


Figure 2. XRD-patterns of air-dried clay fractions of 10 y old batch samples.

References

- Carlson L., Karland O., Oversby V.M., Rance A., Smart N., Snellman M., Vähänen M. & Werme L.O. (2007), *Physics and Chemistry of the Earth* 32, 334-345.
- Milodowski A.E., Cave M.R., Kemp S.J., Taylor H., Vickers B.P., Green K.A., Williams C.L. & Shaw R.A. (2009) SKB Technical report TR-09-02.
- NUMO (2004), NUMO Technical report TR-04-03.
- SKB / Posiva, 2008. Horizontal deposition of canisters for spent nuclear fuel. Summary report of the KBS-3H Project 2004 – 2007. SKB Technical Report TR-08-03. POSIVA 2008-03.