Research paper

Alteration of expandable clays by reaction with iron while being percolated by high brine solutions

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ABSTRACT

Bentonites are suitable candidates as buffer and backfill materials in HLW-repositories. A target of this research is to define the mineralogical alteration of bentonite caused by its interaction with iron powder, which simulates the contact of bentonite with a steel container. Compacted MX80 bentonite and Friedland clay (raw density of 1.6 g/cm^3) were used as the initial materials for clay/iron interaction experiments (10 wt.% of iron) involving percolation with NaCl or Mg-rich IP21 solution. These experiments were conducted at 25 °C, 60 °C, and 90 °C and a suite of analytical techniques was applied to identify the mineralogical transformations. Smectite was the main phase and was fully expandable in all reaction products, though the octahedral and tetrahedral compositions were altered. "Illitization" was found as a main process of smectite alteration and was caused by the percolation component of these experiments. Smectitization occurred only when Fe-oxidation was considerable. The alteration of smectite was mainly driven by the high alkaline pH-value resulting from Fe-corrosion. Different interstratified phases like kaolinite–smectite–dioctahedral vermiculite, berthierine–saponite, chlorite–saponite–trioctahedral vermiculite, and cronstedtite–saponite–trioctahedral vermiculite interstratifications were identified as neo-formed phases which were formed in minor amounts. Cementation of particles by Fe- or Si-precipitation was assumed to reduce swelling pressure and permeability.

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1. Introduction

Compacted bentonites, pure bentonites, and clay–sand mixtures are considered to be important potential engineered barriers for final disposal of high-level radioactive waste in several kinds of geological formations. The slow transport of radionuclides through these barriers is a key boundary condition in long term assessment analyses (Pusch, 1994). Changes of porosity, permeability, and diffusivity can affect the transport of radionuclides. The waste container may be made of iron, copper, carbon steel, or stainless steel depending on the disposal concept, but expandable clays are often considered as the main material of engineered barriers (Arthur et al., 2005; Push, 2003; SKI, 2005; Thorsager and Lindgren, 2004). Nuclear repository concepts must additionally ensure that the heat generated by the nuclear waste does not result in temperatures higher than 100 °C (SKB, 2006). The key question is whether the clay will undergo functionally significant changes over a period of 10,000 years (Sweden concept) or 1 million years (German

concept). Making these factors predictable and quantifiable over the long term requires both lab-scale experiments and mathematical models.

The new phases of Fe-rich sheet silicate formations (Fe-rich serpentine such as cronstedtite, bertherine or Fe-rich chlorite like chamosite) are found in most reports on the interaction between bentonite and iron regardless of the temperature conditions used. Perronnet et al. (2008) and Wilson et al. (2006b) observed that a Fe-rich 7 Å clay mineral was formed at 80 °C which had an iron/clay ratio of approximately 0.3. Pignatelli et al. (2013) reported the appearance of cronstedtite at 60 °C to 90 °C caused by the release of Fe and Si into solution after the dissolution of quartz, T–O–T phyllosilicates, and iron metal. The transformation of smectite to Fe-rich serpentine and chlorite was also reported by Cathelineau et al. (2005), Guillaume et al. (2003, 2004), Lantenois et al. (2005), and Wilson et al. (2006b). Charpentiera et al. (2006), Guillaume et al. (2003, 2004), and Ishidera et al. (2008) detected the newly formed phases of chlorite, vermiculite, saponite, palygorskite, and zeolite as well as the dissolution of smectite by saponization and vermiculization at a wide range of temperature from 80 °C to 300 °C. No mineralogical transformation was detected at 30 °C to 50 °C though the newly formed phases of magnetite, hematite,

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goethite, or even residual Fe were found (Carlson et al., 2007; Osacký et al., 2009; Stríček et al., 2009).

Conversion of smectites to other phases depended upon the initial materials used, the composition of the saturated solutions, the liquid/clay ratio, the iron/clay ratio and on whether the atmosphere consisted of air, argon, or nitrogen as well as on the specific surface of metallic iron (Bourdelle et al., 2014) and the temperature (Pignatelli et al., 2014). Examples of such effects are reported by Perronnet et al. (2008), Mosser-Ruck et al. (2010), Lantenois et al. (2005), de Combarieu et al. (2011), Lantenois et al. (2005), Mosser-Ruck et al. (2010), Osacký et al. (2009), Perronnet et al. (2008), Wilson et al. (2006b). The thermodynamic modeling of metallic iron/clay interactions by Bildstein et al. (2006), Savage et al. (2010a), and Wilson et al. (2006b) predicted the occurrence of Fe-rich silicates under anaerobic conditions and Charpentiera et al. (2006) demonstrated depletion of Si and enrichment of Fe^{3+} in tetrahedral and octahedral sheets, respectively.

In general, the studies of the stability of clays and smectite-rich clays during interaction with Fe under various conditions have indicated that the degree of alteration is sensitive to the time and temperature of exposure, as well as to the composition of the initial solutions, and the ratio of iron/clay or liquid/clay. In particular, dioctahedral smectite was not stable under neutral to alkaline conditions or at a high iron/clay ratio. However, the structural features of smectite, especially the degree of occupancy of the octahedral sheet have not been clearly explained.

Some studies did not detect the transformation of smectite to Fe-rich phases and hence concluded that the Fe/clay interaction would not be an issue in a repository of radioactive waste (Dohrmann et al., 2013; Kaufhold et al., 2013; Madsen, 1998). In several studies, thermodynamic modeling was used to investigate the stability of dioctahedral smectite and these showed that the properties of smectite would be expected to be stable for 10,000 years (Bildstein et al., 2006; Herbert et al., 2011; Montes-H et al., 2005; Savage et al., 2010a) or even for 100,000 years (Marty et al., 2010) regardless of partial transformation of smectite to illite, saponite, vermiculite, or zeolite, and the formation of Fe-rich 1:1 phyllosilicates. These theoretical results are in agreement with the results of laboratory experiments.

In order to evaluate the mineralogical properties of bentonites in the closed system of an underground repository, where corrosion of steel is expected to slowly release iron into the surrounding buffer (compacted bentonite), we have carried out a series of experiments to determine chemical interaction of MX80 bentonite and Friedland clay in contact with native Fe powder (percolated in solutions of NaCl, IP21 — the typical brine encountered in the Zechstein formations in Germany) at 25 °C, 60 °C, and 90 °C. Transmission electron microscopy coupled to energy-dispersive X-ray (TEM-EDX), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and X-ray fluorescence (XRF) were used to identify the chemical–mineralogical properties of the initial materials and products as well as to explain the mineralogical properties of the materials after experiment in terms of the thermodynamic mechanisms driving the alteration of the material.

2. Materials and experiments

2.1. Materials

2.1.1. Clay samples

The experiments were carried out using two potentially expandable buffer clays: (i) MX80 bentonite — a commercial product obtained from the Süd-Chemie AG (Moosburg, Germany); and (ii) Friedland clay taken from the Burgfeld lense (Burgfeld Scholle quarry, Germany) by the drilling core TB1/97 drilled at 8 m sea level in summer 2009 by Mineralische Rohstoffmanagement GmbH — Blautonwerk Company. Both clays were characterized by full expandability. The MX80

bentonite was dominated by montmorillonite, and the Friedland clay contains mainly illite–smectite interstratified structure (IS-ml) and montmorillonite which are all referred to as smectite in this paper.

2.1.2. Solution preparations

The experiments were performed with two solutions of different ionic strength. The first is saturated NaCl solution, a typical brine encountered in the Zechstein formations in Germany (Herbert et al., 2008). The second is IP21 solution, a $MgCl_2$-rich brine, which may be encountered in the Zechstein potash beds in Germany. IP21 is saturated with salt minerals including halite, carnallite, sylvite, kainite, and polyhalite (Herbert et al., 2008). The chemical composition of these brines was determined by Herbert et al. (2008).

2.2. Experiments

The initial MX80 bentonite and Friedland clay were mixed with 10 wt.% of native Fe with grain sizes of 6 to 9 μm and compacted to a density of 1.6 g/cm³. Regardless of the liquid/clay ratio, the compacted materials were percolated using the NaCl and IP21 solutions. In all cases the rate of percolation was 3.9 mL/min. The reaction samples were incubated at 25 °C, 60 °C or 90 °C for 1 month or 2 months as described in Table 1. The different colored zones of the reaction products which may mirror different gradients of Fe-corrosion were also observed (Fig. 1). The reaction products were dialyzed in a 2 mL capsule (semipermeable membrane) for 1 h to remove salt solutions. This experimental design models a dynamic open reaction system.

2.3. Mineralogical analyses

2.3.1. Sampling procedure

Reaction products generated at temperatures of 25 °C and 60 °C showed remarkable Eh-zoning of Fe-activity. Those samples were, therefore, divided into 2 parts: dark gray (assumed to represent high Fe-activity — high content of Fe^{2+}) and brown (probably mirroring lower Fe-activity — low content of Fe^{2+}) (Fig. 1).

2.3.2. Solid characterization

Chemical composition was analyzed using a wavelength-dispersive X-ray Philips PW 2404 spectrometer equipped with a 4 kW Rh X-ray source (10 mA, 20 kV). Samples were milled to <40 μm and analyzed using a non wetting agent and/or oxidizer. Loss on ignition (LOI) was determined at 1100 °C as an approximate measure of volatile H_2O.

For the XRD analysis, specimens of the randomly oriented powder (<40 μm) and oriented mounts (<2 μm fraction) were air dried, treated with ethylene glycolate, and heated (to 550 °C for 4 h) prior to analysis in a Siemens D5000 X-ray diffractometer (Cu Kα radiation, 40 kV, 30 mA, steps of 0.05 °2Θ, and counting time of 10 s). The XRD data were refined by using BGMN-Rietveld software (Kleeberg et al., 2010; Ufer et al., 2008) in cross-checking with the XRF data (Table 2).

The FTIR spectra of bulk samples (milled to <40 μm) were recorded from 400 cm⁻¹ to 4000 cm⁻¹, using a Nicolet 6700 FTIR spectrometer (64 scans, 4 cm⁻¹ resolution). The FTIR-spectra were deconvoluted by Origin Pro Peak Fitting (version 8.5) technique applying Gaussian distribution. The interpretation of individual bands followed Craciun (1984), Farmer and Russell (1974), Goodman et al. (1976), Madejová and Komadel (2001), Madejová et al. (1994), and Russell and Fraser (1994).

Selected individual clay particles were characterized by morphology, crystal habit, chemical composition, electron diffraction, and element distribution using a JEOL JEM-1210 microscope (120 kV, LaB₆ cathode) coupled to an ISIS LINK-OXFORD energy-dispersive X-ray system. Suspensions of clay sample were prepared on carbon-coated Cu-grids by