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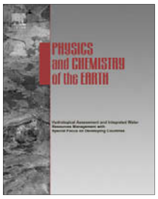

Investigation of montmorillonite alteration and form of iron corrosion products in compacted bentonite in contact with carbon steel for ten years

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ABSTRACT

In high-level radioactive waste disposal, the alteration of montmorillonite due to the corrosion of carbon steel possibly affects the swelling and self-healing capacity of compacted bentonite used as a buffer material. The nature of the corrosion products in compacted bentonite is also important to evaluate not only the diffusion and sorption behavior of radionuclides but also the chemical composition and redox potential of pore water. In this study, the alteration of montmorillonite in compacted bentonite due to the interaction with carbon steel was analyzed by X-ray diffraction (XRD). The possibility of montmorillonite alteration was also investigated from the cation exchange capacity (CEC) of compacted bentonite and scanning electron microscopy (SEM) observation. The corrosion products distributed in the compacted bentonite were investigated by selective dissolution analysis, which can estimate the crystallinity of Fe-bearing compounds. The valence of Fe in the corrosion products was spectrophotometrically determined. From the XRD analysis, newly formed phyllosilicates resulting from the alteration of montmorillonite could not be identified in compacted bentonite. CEC of compacted bentonite adjacent to the carbon steel, in which high concentration of Fe was extracted, was hardly decreased. No significant differences of clay particles were observed with SEM. Thus, the alteration of montmorillonite was scarcely detected in compacted bentonite in contact with carbon steel for ten years. The selective dissolution and valence analyses suggest that most of the corrosion products of carbon steel existed in Kunipia F, which consists of over 95 wt% montmorillonite, was amorphous, non-crystalline or poorly ordered $Fe(OH)_2$. This means that $Fe(OH)_2$ distributed into compacted bentonite was scarcely crystallized within ten years at 80ºC. From the XRD analysis, small amount of green rust one containing Cl^- at the interlayers ($GR1(Cl^-)$) and lepidocrocite were also identified in Kunipia F. Therefore, under this experimental condition, $Fe(OH)_2$ formed in Kunipia F due to the corrosion of carbon steel was oxidized to $GR1(Cl^-)$ as intermediates, and then $GR1(Cl^-)$ was possibly oxidized to lepidocrocite. On the other hand, $GR1(Cl^-)$ was hardly detected in Kunigel V1, which contains 46–49 wt% montmorillonite, from the XRD analysis.

1. Introduction

Long-term safety in the case of geological disposal of high-level radioactive waste (HLW) in Japan is ensured by the multi-barrier system, which consists of an engineered barrier system that includes a vitrified waste, an overpack and a buffer material, and host rock as natural barrier (JNC, 2000). After the disposal repository is closed, the compacted bentonite used as the buffer material saturates with groundwater. Groundwater corrodes the overpack, and subsequently the corrosion products of carbon steel, which is a candidate material for overpack, migrates into the compacted bentonite. Smectite, which is a major component of bentonite, might be altered to other minerals by interactions with the corrosion products. Such an alteration could result in loss of swelling and self-healing capacity. Furthermore, after the overpack has a mechanical failure due to the corrosion, the radionuclides contained in vitrified waste will dissolve into the groundwater and diffuse through the compacted bentonite. The diffusion and sorption behaviors of radionuclides are affected not only by the alteration of smectite but also by the corrosion products migrating into compacted bentonite. Further, the corrosion products affect the chemical composition and redox potential of pore water in compacted bentonite.

The stability of smectite has been reported to be affected by the presence of metal Fe and Fe oxides in aqueous solutions. Lantenois et al. (2005) has investigated the interaction between metal Fe and a variety of natural and synthetic smectite samples at 80 °C by batch experiments and has reported that smectite was destabilized to form newly formed 1:1 phyllosilicate phases (odinite and crondstedtite) under basic pH conditions. Perronnet et al. (2007) has investigated the parameters which influenced Fe(0)–clay

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interactions by batch experiments and has reported that smectite reactivity was possibly affected by the energetic heterogeneity of its edge faces. Wilson et al. (2006b) has investigated the stability of Na-montmorillonite between 80 and 250 °C and reported that Fe-rich smectite, whose swelling property was lower than the montmorillonite starting material, and berthierine was identified at 250 °C. Guillaume et al. (2003) has reported that the alteration of montmorillonite to chlorite and saponite were identified in batch experiments performed at 300 °C in the presence of metallic Fe and magnetite powder in low-salinity solutions. Guillaume et al. (2004) has reported that the alteration of montmorillonite to high-charge trioctahedral Fe^{2+}-rich smectite was found by batch experiments in the presence of magnetite and hematite in low-salinity solutions at 300 °C. However, all these experiments were performed by the batch method. The alteration of smectite in compacted bentonite when it is placed in contact with carbon steel, which represents the simulated condition in a nuclear repository, has not been studied experimentally.

The corrosion product that is thermodynamically stable under expected geological conditions in a repository is magnetite or siderite for groundwater containing high-concentrations of CO_3^{2-} ion (JNC, 2000). Xia et al. (2004) has carried out experiments to study the migration of corrosion products into compacted bentonite from carbon steel under reducing conditions at room temperature and reported that the corrosion product was presumed to be ferrous hydroxide or magnetite. Kozaki et al. (1995) has reported that the corrosion product formed on a pure iron film placed in compacted bentonite was either hydroxide or oxide. Although the corrosion products formed on the carbon steel surface in the presence of compacted bentonite has been thus investigated experimentally and determined to be magnetite or siderite, hydroxide was also expected to be formed on the carbon steel. Ferrous hydroxide possibly increases the concentration of Fe^{2+} in the pore water of compacted bentonite and affects the sorption behavior of radionuclides. Ferrous hydroxide is considered to crystallize on the thermodynamically stable minerals in the long term. However, such crystallization has not been confirmed by experimental studies. Therefore, the mineralogical evolution of ferrous hydroxide in compacted bentonite should be investigated experimentally by long-term corrosion experiment.

In this study, carbon steel was placed in contact with compacted bentonite under anaerobic conditions for ten years at 80 °C. The compacted bentonite was analyzed by X-ray diffraction (XRD) in order to investigate the presence of newly formed phyllosilicates resulting from the alteration of montmorillonite due to its interaction with corrosion products. The oriented samples prepared from the powder of compacted bentonite were analyzed by XRD in order to identify the clay minerals contained in compacted bentonite. The possibility of montmorillonite alteration was also discussed from the cation exchange capacity (CEC) of compacted bentonite and scanning electron microscopy (SEM) observation. The corrosion products distributed in compacted bentonite were investigated by selective dissolution analysis (Stucki et al., 1988), which can estimate the crystallinity of Fe-bearing compounds. The valence of Fe in the corrosion products was spectrophotometrically determined. From these analyses, the corrosion products of carbon steel in compacted bentonite were determined.

2. Experimental

2.1. Materials

The carbon steel used in this study was SM400B (JIS G 3106, ISO 630, rolled steels for welded structure), which is the candidate overpack material. The carbon steel coupons measured 30 × 30 × 2 mm. Each carbon steel coupon was wet-polished with 800-grade grinding papers. The composition of SM400B is listed in Table 1.

Table 1
Composition of trace amount element in SM400B.

Elements	C	Mn	Si	S	P
Content (%)	0.13	0.69	0.19	0.007	0.011

The bentonites used were Kunipia F® and Kunigel V1® (Kunimine Industries Co. Ltd.). The chemical compositions of these bentonites are listed in Table 2. Kunipia F is a purified montmorillonite sample made from Kunigel V1 and consists of over 95 wt% montmorillonite (Ito et al., 1993). The structural formula of the montmorillonite is: $(Na_{0.42}K_{0.008}Ca_{0.068})(Si_{3.91}Al_{0.09})(Al_{1.56}Mg_{0.31}Fe^{III}{}_{0.09}Fe^{II}{}_{0.01})O_{10}(OH)_2$. Kunigel V1 consists of 46–49 wt% montmorillonite, 37–38 wt% chalcedony and a few wt% of minor minerals, i.e., plagioclase, calcite, dolomite, analcime and pyrite (Ito et al., 1993). Kunipia F and Kunigel V1 were compacted to dry densities of 1.8 g/cm^3.

Simulated sea water (SW), simulated sea water containing a high concentration of carbonate (SWC) and low-saline solution (LS) were used for the experiment. The composition of the SW, SWC and LS is listed in Table 3. The SWC was prepared by adding $NaHCO_3$ to 5.6×10^{-1} mol/dm^3 of NaCl until the concentration of $NaHCO_3$ was 1.0×10^{-1} mol/dm^3. The LS contained 2.5×10^{-3} mol/dm^3 of $NaHCO_3$ and NaCl. The initial pHs of the SW, SWC and LS were 7.9, 8.7 and 9.1, respectively. These solutions were prepared from deionized water degassed in an N_2 glove box, in which the concentrations of O_2 and CO_2 were maintained lower than 1 ppm.

Fig. 1 schematically shows the titanium column used in this study. The column consists of upper and lower lids and a sample holder between the lids and filters. The sample holder has a cylindrical sample compartment (diameter, 42 mm and thickness, 14 mm), in which carbon steel coupon is placed and bentonite is compacted. The carbon steel coupons were positioned at the center of the compacted bentonite. A ceramic filter is placed on each side of the bentonite sample in order to avoid loss of material from the bentonite during the experiment. The upper and lower lids have an opening through which the solution was allowed to soak into the compacted bentonite. The column was completely immersed in the solution during the experiment.

2.2. Procedures

The column was immersed for ten years in an N_2 glove box. The column into which Kunipia F was compacted was immersed in SW at 80 °C. The columns into which Kunigel V1 was compacted were immersed in SW, SWC and LS at 80 °C. After ten years, the column was frozen in liquid nitrogen following which the compacted bentonite was removed from the column. The frozen compacted bentonite was removed from the carbon steel coupon by a hammer. The compacted bentonite was sliced into sections from the surface in contact with carbon steel. XRD, SEM, CEC, selective dissolution and valence analyses were carried out on the sections. The procedures for these analyses are described in Section 2.3, Section 2.4, Section 2.5, and Section 2.6. All procedures after the compaction of bentonite were performed in an N_2 glove box.

2.3. Procedures for XRD analysis

The compacted bentonite was sliced into sections having thickness ranging from 0.2 to 1.0 mm. The sections were dried at room temperature and then ground into powder. The bentonite powders were pressed onto silicone plates and analyzed by XRD (Rigaku