INVESTIGATION OF SMECTITE ALTERATION AND FORM OF IRON CORROSION PRODUCTS IN COMPACTED BENTONITE BEING IN CONTACT WITH CARBON STEEL FOR TEN YEARS

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INTRODUCTION

In high-level radioactive waste disposal, an overpack, into which vitrified waste is placed, is planed to be surrounded by a layer of compacted bentonite. After the disposal repository is closed, groundwater will corrode the carbon steel overpack and then the corrosion products of carbon steel will migrate into compacted bentonite. Therefore, alteration of smectite, which is a major constituent mineral of bentonite, may occur due to chemical interaction with the corrosion products. After mechanical failure of overpack because of the corrosion, radionuclides contained in vitrified waste will dissolve into the groundwater and diffuse through the compacted bentonite. Diffusion behavior of radionuclides is possibly affected also by the corrosion products which migrate into compacted bentonite and altered smectite.

In this study, carbon steel was placed into compacted bentonite under low-oxygen condition for about ten years at 80°C. Swelling characteristics of the bentonite were observed by X-ray diffractometry (XRD) using oriented samples from clay fractions of the bentonite, before and after treatment with ethylene glycol. Furthermore, the corrosion products migrating into the compacted bentonite were investigated by the selective dissolution analysis (Stucki, J. W., 1988), which can estimate the crystallinity of Fe-bearing compounds. The valence of Fe in corrosion products was spectrophotometrically determined.

EXPERIMENTAL CONCEPT

The bentonite used in this study was Kunigel V¹ (Kunimine Industries Co. Ltd.). Kunigel V1 was compacted into a column (42 mm in diameter and 14 mm in thickness) to obtain a dry density of 1.8 Mg/m³. The carbon steel (SM400B) was placed into the middle of compacted bentonite. The shape of carbon steel was 30x30 mm square and 4 mm in thickness. Three different component solutions, simulated sea water, simulated sea water containing high concentration of carbonate (0.1 mol/dm³ HCO₃⁻) and low-saline solution (2.5x10⁻³ mol/dm³ HCO₃⁻, 2.5x10⁻³ mol/dm³ Cl⁻ and 5.0x10⁻¹ mol/dm³ Na⁺), were prepared to immerse the columns. Most of the columns were placed at 80°C in N₂ glove box, in which the concentrations of O₂ were lower than 1 ppm, while some columns immersed in simulated sea water were placed at 50°C. After the columns were left for about 10 years, the columns were taken apart. The bentonite surface with which the carbon steel was in contact was directly analyzed by XRD and then scraped off. The scraped bentonite was dried and ground into powder by a mortar. The ground powder was dispersed in deionized water and then a small amount of the supernatant was dropped onto silicone plates. These oriented samples were analyzed by XRD before and after treatment with ethylene glycol. Furthermore, the compacted bentonite was sliced into sections. To extract Fe²⁺ and Fe³⁺ from the pore water of compacted bentonite, 1 mol/dm³ NH₄Cl solution was added to the bentonite slices and then concentration of Fe in the supernatants was measured after centrifuging. After the residual supernatant was removed, 0.15 mol/dm³ sodium oxalate solution adjusted to pH 3.5 was added in order to extract amorphous, non-crystalline or
poorly ordered Fe compounds. After the oxalate extraction, 1 mol/dm$^3$ HCl solution was added to extract comparatively crystallized Fe compounds. The valences of iron in each supernatant were analyzed spectrophotometrically.

RESULTS AND INTERPRETATION
Corrosion products of siderite and ankerite were detected by the XRD analysis on surface of all bentonite samples. No crystalline minerals which originated from alteration of smectite were found. Figure 1 shows the XRD profiles of oriented samples of bentonite immersed in simulated sea water at 80°C before and after treatment with ethylene glycol. The diffraction peak was found at 7.2°, which corresponded to 1.23 nm of basal spacing of smectite, before ethylene glycol treatment, while the peak was found at 5.2°, which corresponded to 1.70 nm, after the treatment. The shift of diffraction peak was also found for the other bentonite samples. This result indicates that the swelling property of bentonite was maintained for about 10 years, and therefore alteration of smectite was scarcely occurred in compacted bentonite.

Figure 2 shows the results of selective dissolution analysis. The concentration profiles of Fe obtained from NH$_4$Cl, oxalate and HCl extractions are expressed as Fe-NH$_4$Cl, Fe-Oxalate and Fe-HCl, respectively. Fe-Total indicates the sum of concentrations of Fe obtained from these three extractions. Most of the corrosion products in compacted bentonite was extracted by oxalate, while HCl extractions scarcely abstracted the corrosion products. Furthermore, most of the corrosion products was found to be bivalent from the results of valence analysis by spectrophotometer. These results suggests that the corrosion products which distribute in the compacted bentonite from carbon steel mostly exist as amorphous, non-crystalline or poorly ordered bivalent Fe compounds.

References: