

# Microbial Effects of the Alteration of KJ-II Bentonite Containing a Corrosion Product ( $\text{Fe}_2\text{O}_3$ ) Under Anaerobic Alkaline Conditions

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## 1. Introduction

The underground disposal sites of high-level radioactive wastes are mostly an anaerobic environment. There are various native microbes involving sulfate-reducing bacteria (SRB) in deep underground environments, and they could cause oxidation-reduction changes of groundwater through biochemical metabolism. It has been reported that the activity of microbes can affect the corrosion of metal canisters that are used to protect high-level radioactive wastes. The metal corrosion products can be also altered by underground water and radiation for a long time. The alteration can make them release some metal ions, for example, copper (Cu) and iron (Fe), which are the main materials of the corrosion products. These metal ions can replace some cation ions that exist between clay layers of bentonite, which are the buffer material. This alternation of bentonite may affect the chemical behavior of radionuclides, diffusing from it.

In this study, we investigated the effect of microbial activity on the alternation of KJ-II (Gyeongju) bentonite with corrosion products under anaerobic alkaline environment, which is very similar to the actual disposal site.

## 2. Materials and methods

### 2.1 Materials

The bentonite used in this study was taken from Gyeongju. We named it as “KJ-II bentonite” (Clariant Chemicals Korea Ltd.). It is a Ca-type bentonite with its ratio of CaO :  $\text{Na}_2\text{O}$  as 5.5:1, containing montmorillonite with > 65% in its total amount [1]. The KJ-II bentonite was mixed with hematite ( $\text{Fe}_2\text{O}_3$ ) powder (10% w/w) that can be one of the corrosion products of the metal canister.

Distilled water sterilized was added to the KJ-II bentonite to make a solid-liquid ratio (S/L) to be 1 g/30 ml in a centrifuge tube of 50 ml. To remove some oxygen in the bentonite, it was saturated and shaken for 3 days (120 rpm, 30°C). Finally, the

supernatant was removed after centrifugation (10,000 rpm, 5 minutes).

In the clean bench, Cesium (Cs) solution of 1000 ppm (mg-Cs/L) was prepared to know its adsorption amount onto the bentonite. Distilled water and cesium solution were purged with  $\text{N}_2$  gas for 40 minutes to remove oxygen in the solution.

### 2.2 Methods

An experiment was conducted under anaerobic conditions using the glove box filled with  $\text{N}_2$  gas. The prepared distilled water was poured into centrifuge tube containing bentonite. The cesium solution was added into it to be 20 ppm-Cs by filtering 0.20  $\mu\text{m}$  (ADVANTEC). NaOH solution was used to adjust the pH of the solution media as 9. The experiments were carried out for 3 months. After 3 months, the remaining solution was centrifuged (10,000 rpm, 5 minutes), and the precipitated solid samples were analyzed by XRD (X-ray diffraction) and SEM (scanning electron microscope) to detect some secondary products from the alteration of bentonite.

## 3. Results and discussion

### 3.1 Changes of chemical compositions

The supernatant of bentonite was extracted and analyzed to examine the concentrations of Ca and Cs by using ICP-MS (inductively coupled plasma mass spectrometer). The result shows that the concentration of Ca has increased under anaerobic condition (Fig. 1(a)). On the other hand, another sample did not show the increase of Ca under aerobic condition. During the experiment, the hematite in the bentonite was reduced under anaerobic condition, causing  $\text{Fe}^{3+}$  ions of the hematite to be  $\text{Fe}^{2+}$  ions. In addition, structural  $\text{Fe}^{3+}$  bioreduction to  $\text{Fe}^{2+}$  by SRB that are surviving in the bentonite may promote to release Fe ions from the bentonite. As a result, interlayer  $\text{Ca}^{2+}$  ions in the bentonite can be

exchanged with  $\text{Fe}^{2+}$  ions. These processes can affect the bentonite [2].

The alternation can also affect the adsorption of radionuclides. The adsorption of Cs ions was relatively faster under aerobic condition (Fig. 1(b)). The adsorption amount of Cs ions was about 4.2% higher under aerobic condition than under anaerobic condition. It demonstrated that the alternation of bentonite interferes with the adsorption of Cs onto bentonite under anaerobic condition.

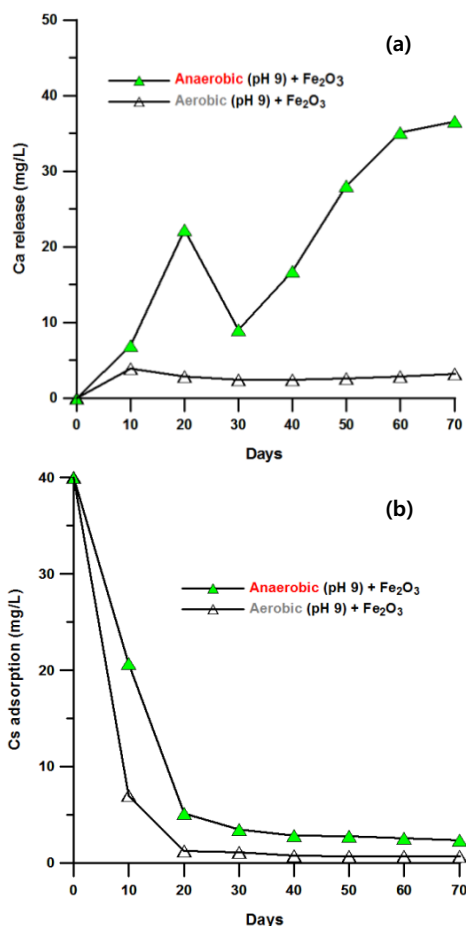


Fig. 1. (a) Concentrations of Ca ions released from bentonite and (b) Cs adsorption onto KJ-II bentonite with  $\text{Fe}_2\text{O}_3$  under anaerobic or aerobic conditions.

### 3.2 Formation of secondary minerals

$\text{CaCO}_3$  (calcite), a secondary mineral, was formed under anaerobic conditions in Fig. 2. The generation of the secondary mineral was also found in the SEM analysis. It is assumed that the presence of the newly formed  $\text{CaCO}_3$  materials on the bentonite surface interrupted the adsorption of Cs ions. In addition, the decrease of d-spacing was caused by the exchange of Fe ions (atomic radius: 140 pm) for Ca ions (atomic radius: 180 pm).

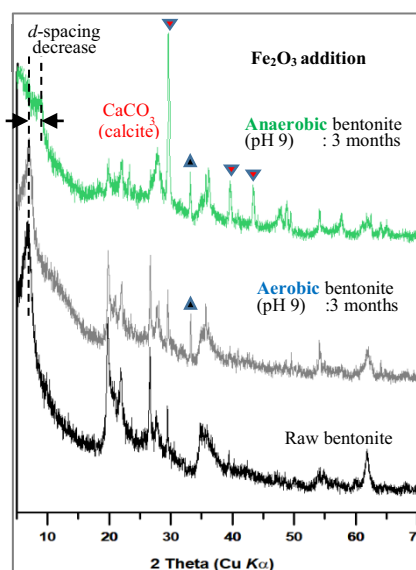


Fig. 2. X-ray diffraction patterns of bentonites with  $\text{Fe}_2\text{O}_3$  under anaerobic and aerobic conditions.

## 4. Conclusion

The effect of microbial activity was investigated under anaerobic alkaline conditions. In this study, the calcite, a secondary mineral, was found in the KJ-II bentonite with  $\text{Fe}_2\text{O}_3$ , which was altered during the experiment. It seems that the secondary mineral prevents Cs from adsorbing onto the bentonite. In the natural disposal site, therefore, the corrosion products of canister may affect the long-term behaviors of radionuclides in the altered bentonite with microbes.

## ACKNOWLEDGEMENT

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## REFERENCES

- [1] Yoo, M., et al., "Measurement of Properties of Domestic Bentonite for a Buffer of an HLW Repository", JNFCWT, 14(2), 135-147 (2016).
- [2] Jing Zhang, et al., "Microbial reduction of Fe(III) in smectite minerals by thermophilic methanogen Methanothermobacter thermoautotrophicus", Geochim. Cosmochim. Acta, 106, 203-215 (2013).