

Influence of Microbial Activity on the Long-Term Alteration of Compacted Bentonite/Metal Chip Blocks

Seung Yeop Lee*, Jae-Kwang Lee, and Jang-Soon Kwon

Korea Atomic Energy Research Institute, 111, Daedeok-daero 989 beon-gil, Yuseong-gu, Daejeon 34057, Republic of Korea

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Safe storage of spent nuclear fuel in deep underground repositories necessitates an understanding of the long-term alteration of metal canisters and buffer materials. A small-scale laboratory alteration test was performed on metal (Cu or Fe) chips embedded in compacted bentonite blocks placed in anaerobic water for 1 year. Lactate, sulfate, and bacteria were separately added to the water to promote biochemical reactions in the system. The bentonite blocks immersed in the water were dismantled after 1 year, showing that their alteration was insignificant. However, the Cu chip exhibited some microscopic etch pits on its surface, wherein a slight sulfur component was detected. Overall, the Fe chip was more corroded than the Cu chip under the same conditions. The secondary phase of the Fe chip was locally found as carbonate materials, such as siderite (FeCO_3) and calcite ($(\text{Ca}, \text{Fe})\text{CO}_3$). These secondary products can imply that the local carbonate occurrence on the Fe chip may be initiated and developed by an evolution (alteration) of bentonite and a diffusive provision of biogenic CO_2 gas. These laboratory scale results suggest that the actual long-term alteration of metal canisters/bentonite blocks in the engineered barrier could be possible by microbial activities.

Keywords: Repositories, Alteration, Canisters, Bentonite, Bacteria

*Corresponding Author.

Seung Yeop Lee, Korea Atomic Energy Research Institute, E-mail: seungylee@kaeri.re.kr, Tel: +82-42-868-4735

ORCID

Seung Yeop Lee
Jang-Soon Kwon

<http://orcid.org/0000-0002-0388-2315>
<http://orcid.org/0000-0002-1826-6443>

Jae-Kwang Lee

<http://orcid.org/0000-0003-3903-0904>

1. Introduction

In order to dispose the high-level radioactive wastes (HLRW) in a deep underground repository site, metal canisters and buffer materials are necessarily needed [1]. Among buffer materials, bentonite is chiefly considered as one of the buffer candidates. Various metal canisters that can safely keep and contain the spent nuclear fuel have been currently developed [2, 3], and some candidate metallic materials have been tested for their ductility, strength, and other physical characteristics. In the physical tests, a corrosion resistance of metallic material is a very important factor because such a metal corrosion can cause gradual transformation, physical changes (e.g., lowering strength), and chemical/mineralogical alterations of metallic materials. Due to these reasons, metal corrosion tests should be performed in advance before applying metallic materials to industrial fields [4-6]. However, corrosion tests for the metallic materials have been mostly conducted under aerobic conditions.

Considering the underground HLRW disposal environments, we need to get some data and understanding of the metal corrosion occurring under reducing or anaerobic conditions. Recently, several metal corrosion tests and experiments were conducted under anoxic or anaerobic conditions [4, 7-10]. However, specific data and information for a metallic corrosion occurring inside a compacted bentonite block have been rarely reported to date.

Several studies show that there are diverse bacteria that live in groundwater as well as rock-fractures, largely affecting the underground redox reaction [11-13]. Among the anaerobic bacteria, sulfate-reducing bacteria (SRB) are known to have an ability to reduce sulfate to sulfide using electron donors (e.g., lactate, H₂ gas). There are some reports that the SRB also exist in natural bentonite and could be activated if electron donors and electron acceptors are properly provided [14, 15].

In this study, we want to investigate microbial effects on the alteration of compacted bentonite and metal

canisters not in general underground environments but in specific ones. We performed a laboratory long-term metal corrosion test by embedding Fe or Cu metal chip in a compacted bentonite block, which has been placed in various anaerobic water for 1 year. In the experiment, we focused on an anaerobic microbial metal alteration (corrosion) by directly loading aqueous SRB or by indirectly activating the indigenous bentonite SRB through a supply of lactate (electron donor) and sulfate (electron acceptor) to the saturating water. We also attempted to know how the evolution (alteration) of bentonite and the corrosion of metal chip can be geochemically affected by the anaerobic waters for a long time.

2. Experimental

2.1 Materials and Experimental Conditions

We prepared Kyungju bentonite blocks that were highly compacted with 1.6 g·cm⁻³ in a cylindrical form with 20 mm in height and 30 mm in diameter (Fig. 1(a)). Before compacting the bentonite in a cylindrical block, we inserted iron or copper metal chip (thin metal foil, Aldrich) in each center of a powdered bentonite. The metal chip was like a square plate that had 1×1 cm in size and 0.1–0.3 mm in thickness. The compacted bentonite block with metal chip was thrust into an open acryl capsule with cylindrical form and tightly covered with SUS (stainless steel) micro-net (30-μm in pore size) and porous acryl plate (Fig. 1(b)). We put the capsule (shielding the bentonite block) in a glass container (500 ml) to be submerged under anaerobic water provided. Subsequently, the glass container was capped with a Teflon-lined PP lid. Finally, the glass container with the capsule was placed in a glove box filled with a mixed gas (N₂:CO₂ = 80:20) for 1 year.

We prepared 3 kinds of anaerobic waters to be used in the experiment. The prepared anaerobic waters are as follows: pure water (N₂-purged distilled water), KURT

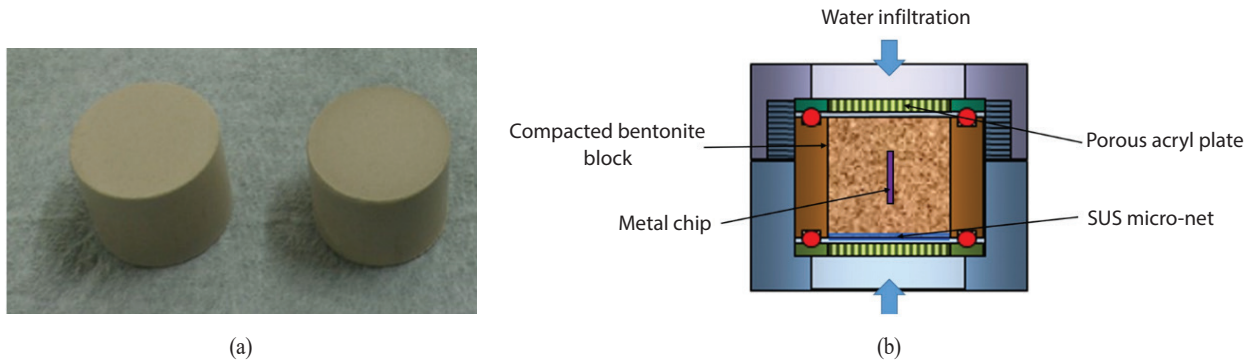


Fig. 1. (a) Compacted Kyungju bentonite blocks. (b) Conceptual image of an open acrylic capsule shielding a compacted bentonite block and inside metal (Cu or Fe) chip.

(KAERI underground research tunnel) groundwater, and nutrient medium. The KURT groundwater was collected from a depth of approximately -230 m at DB-01(i6) bore-hole in the KURT. Its aqueous properties and chemical compositions were previously reported by Lee et al. [16]. The nutrient medium was used to enrich indigenous SRB in the Kyungju bentonite, and its preparation method was already reported by Oh et al. [17]. It basically has aqueous iron(II) and sulfate components in its medium contents.

2.2 Experimental Settings for the Interaction of Water-Bentonite/Metal Block

We prepared two water-bentonite/metal block interaction sets on the basis of using different anaerobic waters. First, Set I basically used natural KURT groundwater as a reacting water for some bentonite/Cu chip blocks for 1 year. To promote a biochemical interaction between the KURT groundwater and the bentonite/Cu chip block, Na-lactate, Fe-sulfate, and a KURT bacterium [18] were additionally added to the KURT groundwater, making four different subsets. The subsets are as follows: 1. KURT groundwater (200 ml), 2. KURT groundwater + Na-lactate (10 mM), 3. KURT groundwater + Na-lactate + Fe-sulfate (2 mM), 4. KURT groundwater + Na-lactate + Fe-sulfate + KURT SRB (5 ml; $1.5 \text{ mg protein} \cdot \text{L}^{-1}$). The injected Na-lactate and the Fe-sulfate were intended to play as an electron donor and

an electron acceptor, respectively. The injected KURT SRB was provided via a sequential cultivation of the SRB living in the KURT groundwater [16].

Secondly, Set II used pure (distilled and sterilized) water and nutrient medium instead of the KURT groundwater to interact with the bentonite blocks with metal (Fe or Cu) chip for 1 year. Its subsets are as follows: 1. Cu-bentonite + nutrient medium (250 ml), 2. Fe-bentonite + nutrient medium, 3. Cu-bentonite + pure water (250 ml), 4. Fe-bentonite + pure water. As previously mentioned, the nutrient medium had iron(II) and sulfate components and was used to activate indigenous SRB in the Kyungju bentonite.

2.3 Analytical Technique

After 1 year, the capsules that have tightly shielded the bentonite blocks were dismantled in the anaerobic glove box. We carefully cut the bentonite blocks into halves with a knife to take out metal chips embedded in them. To prevent the sample oxidation, this dismantling process was all carried out in the glove box. The metal chips obtained had little clay remnants on their surfaces, and they were frozen and freeze-dried for 24 hours using a freeze-drier (Bondiro, Ilshin Co.). We microscopically examined the metal chips using field emission scanning electron microscopy (FESEM; S-4700, Hitach) to acquire useful information about their long-term corrosion characteristics and

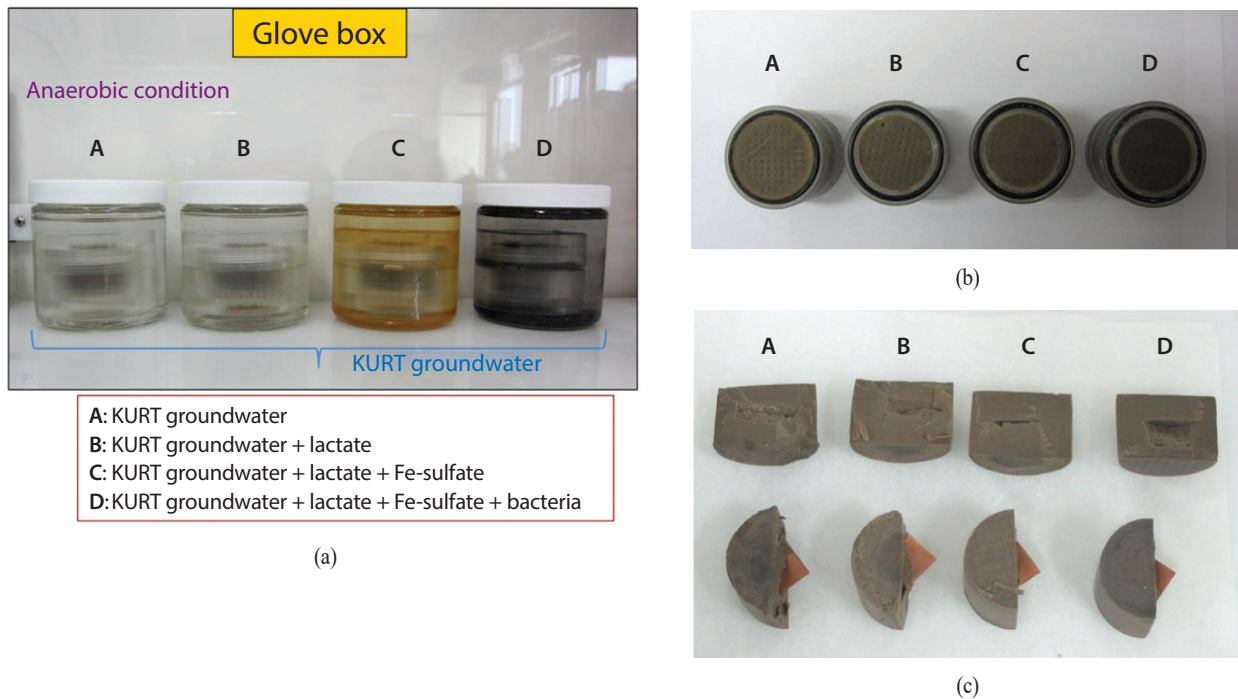


Fig. 2. An experimental Set I for the interaction of KURT groundwater-bentonite/Cu chip block.
 (a) Four bentonite/Cu chip blocks immersed in the KURT groundwater with additives in glass containers under an anaerobic condition.
 (b) The anaerobically dried bentonite blocks of (a). (c) The sectioned bentonite blocks of (b).

byproducts. For the FESEM observation, metal samples were dried in an anaerobic chamber for several hours and then uniformly sprayed on a carbon tape pasted on the specimen holder. In order to avoid charging during observation, the samples were coated with a thin OsO_4 (~10 nm) layer. Chemical analysis on the metal chip was also carried out using an energy dispersive X-ray spectrometer (EDS; EMAX, Horiba).

3. Results and Discussion

3.1 Cu Corrosion by Permeation of KURT Groundwater

As an interaction between the KURT groundwater and the bentonite/Cu chip blocks progresses, there has been gradual color changes in water (Fig. 2). Especially, the

groundwater of sample D turned to black in its color, probably due to an influence of the sulfide enrichment by SRB activity. After 1 year, we took all the bentonite blocks (out of the capsule) and dried them (Fig. 2(b)). Two bentonite blocks (C and D) appeared to be relatively darker than the others (A and B). However, most copper metal chips embedded in the bentonite blocks revealed little corrosion features when observed with the naked eye (Fig. 2(c)). It means that it is not easy for a copper corrosion (alteration) to widely occur in the engineered barrier even under a large microbial sulfide generation.

The copper chips that were embedded in the bentonite blocks were dried under an anaerobic condition and investigated by using FESEM. A copper chip from sample D appeared to have numerous etch pits on its surface as microscopically investigated (Fig. 3). The sizes of etch pits were largely different from ~nm to several ~ μm in length. An enlarged view of a specific etch pit (Fig. 3(b)) shows

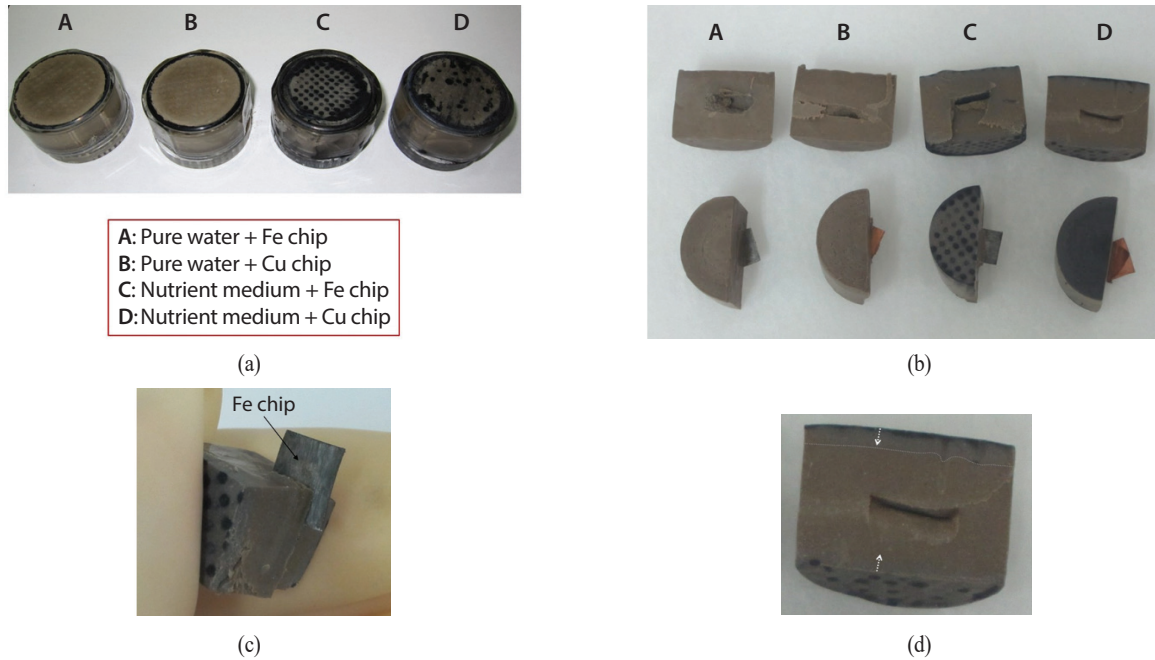


Fig. 5. An experimental Set II for the interaction of synthetic water-bentonite/metal (Fe or Cu) chip block. (a) Anaerobically dried bentonite/metal chip blocks. (b) The sectioned bentonite blocks of (a). (c) Enlarged view of a Fe chip from sample C in (b). (d) Enlarged view of the sectioned bentonite block D in (b). Arrows indicate the alteration depth of the bentonite block by a sulfide diffusion.

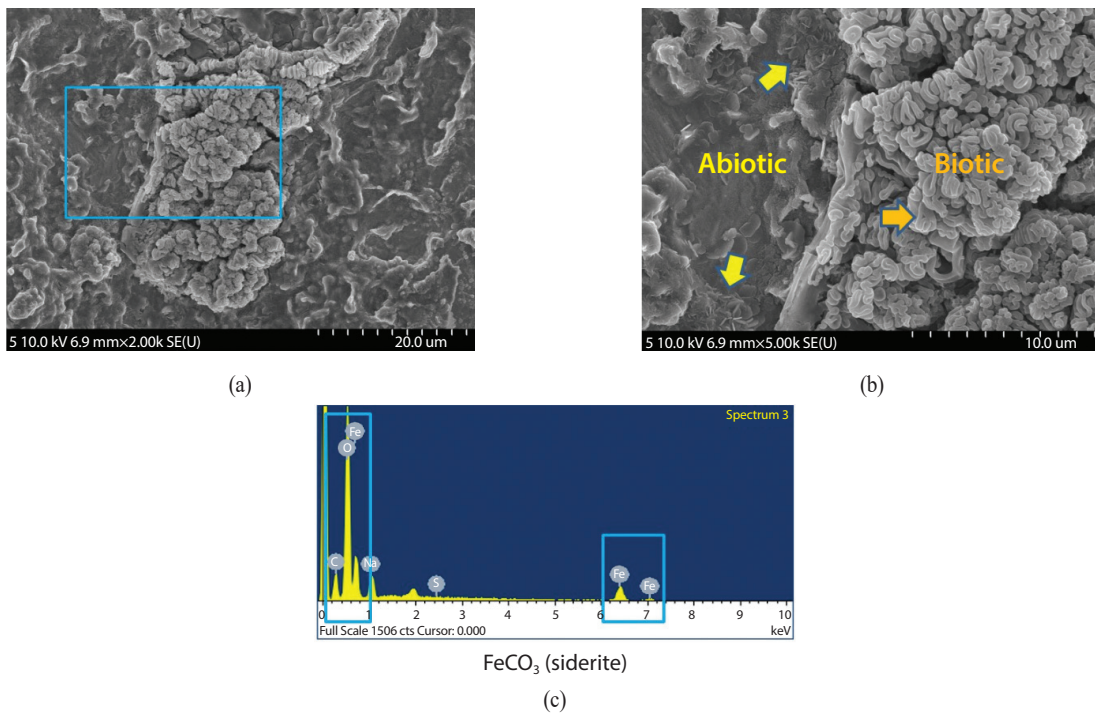


Fig. 6. Microscopic examination on the Fe chip from sample A in Fig. 5. (a) FESEM image of the Fe chip surface with locally different FeCO₃ materials. (b) Enlarged view of a square in (a). Arrows indicate secondary FeCO₃ materials formed on the Fe chip surface. (c) EDS spectrum showing major components of (b).

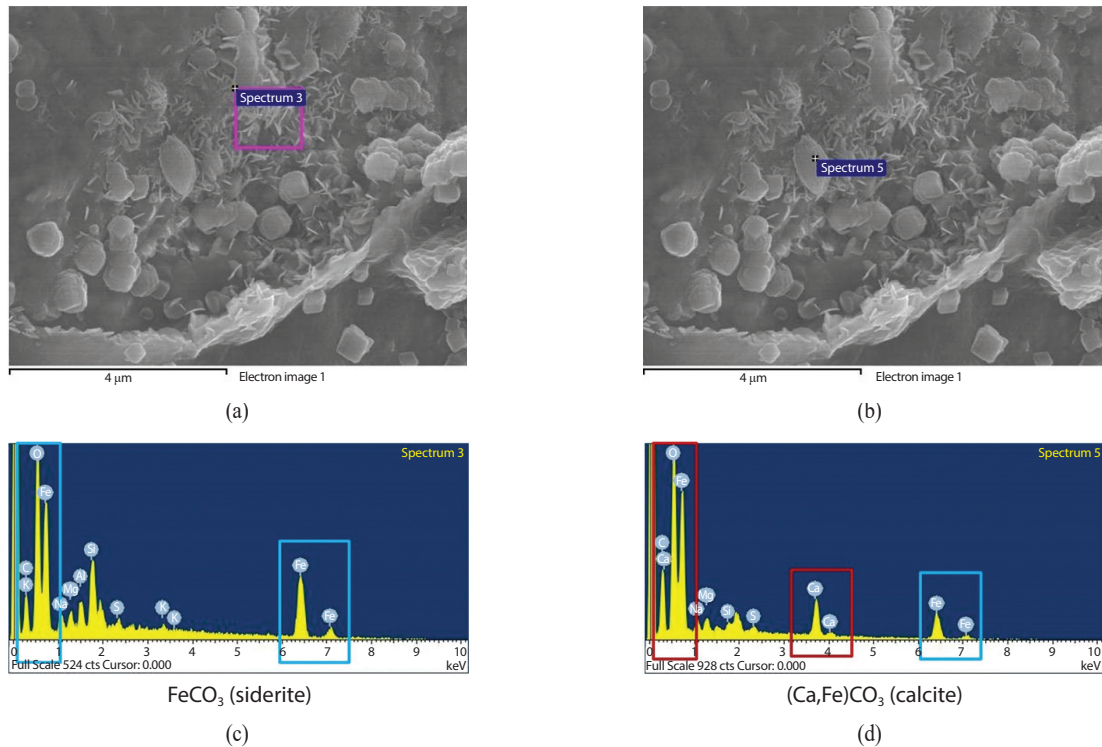


Fig. 7. Microscopic examination on the Fe chip from sample C in Fig. 5. (a) and (b) FESEM images of the Fe chip surface with locally different carbonate phases. (c) EDS spectrum analyzed for a square area in (a). (d) EDS spectrum analyzed for a point area in (b).

3.2 Fe/Cu Corrosion by Permeation of Synthetic Water

For the Set II samples that had been evolved in the pure (distilled) water or the nutrient medium for 1 year, we examined their bentonite blocks and metal chips (Fig. 5). Before saturating the bentonite blocks, copper or iron metal chips were embedded into them in advance. The evolved bentonite blocks were different in colors on their surfaces. In particular, two bentonite blocks (C and D) were much darker than the others (A and B) (Fig. 5(a)). As they were cut in half, we found out that iron chips were relatively more corroded as compared to copper ones (Fig. 5(b)). For example, an iron chip from sample C, which was preserved in nutrient medium, shows that its surface was largely corroded and stained with black and white colored materials (Fig. 5(c)).

It seems that the metal corrosion in the bentonite block

may be facilitated by gases diffusing from the bacterial metabolism. Microbial metabolism in the groundwater or anaerobic water could produce gases, such as CO_2 and H_2S , and enrich them (around the bentonite block). In particular, SRB among various anaerobic bacteria can generate a significant quantity of H_2S (or HS^-) via the microbial reduction of sulfate (SO_4^{2-}) in water, depending on the amount of electron donors (e.g., lactate, H_2) [10, 14, 16]. We believe that microbial gases, such as H_2S and CO_2 , could gradually penetrate into the compacted bentonite block. Fig. 5(d) evidently shows the gradual infiltration of sulfidic gas (or aqueous HS^-) into the bentonite block with a diffusion rate of 2–3 mm/year. Its inner diffusion depth/area is relatively darker in color than the core of the bentonite block.

We microscopically examined the iron chips from the bentonite blocks in Fig. 5. The iron chip from sample A was investigated using FESEM and EDS (Fig. 6), and its surface

was revealed to be partly coated with secondarily formed Fe-carbonate materials. Most of them was identified as FeCO_3 (Fig. 6(c)). Interestingly, it appeared to have two completely different shapes (Fig. 6(b)). This suggests that the origin of FeCO_3 may be different. We assume that the FeCO_3 phase might have been produced in different ways: biotic or abiotic processes. It is likely that if biotic process was locally superior to abiotic one, a certain portion of FeCO_3 may appear to be amorphous or wormlike in its morphology.

For another sample C in Fig. 5, which has been preserved in a nutrient medium for 1 year, we microscopically examined its iron chip surface (Fig. 7). We found out that the iron chip locally had siderite (FeCO_3) and calcite (CaCO_3) on its surface. Interestingly, most calcite observed was relatively bigger than siderite in size, featuring a rhombohedral habit. Furthermore, it was not completely pure in its chemical composition where Ca^{2+} was partly replaced by Fe^{2+} (Fig. 7(d)). We believe that the calcite formation may be largely influenced by the microbial activity. As previously mentioned, the microbial activity can be highly facilitated in a nutrient medium, resulting in a significant production of CO_2 gas. The enriched CO_2 gas can diffuse into the bentonite block and facilitate the corrosion of the embedded metal (iron) chip. Through this process, the biogenic CO_2 gas could involve in the calcite formation around the iron chip surface. It is assumed that a significant amount of Ca^{2+} in the calcite formation may be derived from the Ca-type montmorillonite interlayers. The interlayer Ca^{2+} ions can be readily exchanged with the Fe^{2+} ions released from the iron chip, resulting in serving the calcite formation. As a result, it seems that a significant amount of calcite could be possibly made around the iron chip surface, forming a secondary solid solution, $(\text{Ca}, \text{Fe})\text{CO}_3$, under the condition of continuous Fe^{2+} leaching.

4. Conclusions

A yearly alteration of the bentonite/Cu chip blocks

by the permeation of KURT groundwater or synthetic water was not significant. However, the Cu chip had some nanoscale etch pits on its surface where sulfur was detected and regarded as a major cause for its corrosion. The iron chip was more corroded than the copper one under the same anaerobic conditions. In particular, the iron's secondary corroded phase was locally found as carbonate materials, such as siderite (FeCO_3) and calcite ($(\text{Ca}, \text{Fe})\text{CO}_3$). It suggests that the local generation of the secondary carbonate phase was evidently influenced by the biogenic CO_2 gas in our system. Our results can thus imply that the long-term corrosion of metal canisters in the engineered barrier may be possible by the influence of microbial activity.

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