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Biogeochemical changes at early stage after the closure of radioactive waste geological repository in South Korea

Sungwook Choung [a], Wooyong Um [a,b,*], Seho Choi [a], Arokiasamy J. Francis [a,c], Sungpyo Kim [d], Jin beak Park [e], Suk-Hoon Kim [f]

[a] Division of Advanced Nuclear Engineering, Pohang University of Science and Technology (POSTECH), 77 Chongam-ro, Nam-gu, Pohang 790-784, Republic of Korea
[b] Energy and Environment Directorate, Pacific Northwest National Laboratory (PNNL), 902 Battelle Blvd., P7-54, Richland, WA 99354, USA
[c] Environmental Sciences Department, Brookhaven National Laboratory, Upton, NY 11973, USA
[d] Department of Environmental Engineering, Korea University, 2511 Sejong-ro, Sejong 339-700, Republic of Korea
[e] Korea Radioactive Waste Agency (KORAD), 111, Daedeok-daero 989 beon-gil, Yuseong-gu, Daejeon 305-353, Republic of Korea
[f] FNC Technology Co., 135-306, Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul 110-799, Republic of Korea

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A B S T R A C T

Permanent disposal of low- and intermediate-level radioactive wastes in the subterranean environment has been the preferred method of many countries, including Korea. A safety issue after the closure of a geological repository is that biodegradation of organic materials due to microbial activities generates gases that lead to overpressure of the waste containers in the repository and its disintegration with the release of radionuclides. As part of an ongoing large-scale in situ experiment using organic wastes and groundwater to simulate geological radioactive waste repository conditions, we investigated the geochemical alteration and microbial activities at an early stage (~63 days) intended to be representative of the initial period after repository closure. The increased numbers of both aerobes and facultative anaerobes in waste effluents indicate that oxygen content could be the most significant parameter to control biogeochemical conditions at very early periods of reaction (<35 days). Accordingly, the values of dissolved oxygen and redox potential were decreased. The activation of anaerobes after 35 days was supported by the increased concentration to ~50 mg L^{-1} of ethanol. These results suggest that the biogeochemical conditions were rapidly altered to more reducing and anaerobic conditions within the initial 2 months after repository closure. Although no gases were detected during the study, activated anaerobic microbes will play more important role in gas generation over the long term.

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1. Introduction

A major environmental concern in radioactive waste management is the potential release and transport of radionuclides to the biosphere after the closure of underground radioactive waste disposal facilities. Scientists and engineers have been considering numerous scenarios regarding the assessment of the performance of geological repository over a very long time. A starting point of the scenarios is that the repository may be saturated by local groundwater soon after facility closure. This could lead to changes in background geochemical conditions such as pH and oxidation–reduction potential (ORP) in the geological repository. In addition, intrusion of groundwater to the repository could introduce microbial activities, because a variety of indigenous microorganisms are likely present in both groundwater and the wastes as well as organisms introduced during the repository construction and operation phases.

One of the main safety issues in the repository is potential gas generation by microbial activities under saturated groundwater conditions. The generated gas builds up pressure in the repository, which may result in the loss of integrity of the waste containers and the repository, and facilitate radionuclide transport through the groundwater system (Small et al., 2008; Stroes-Gascoyne and West, 1996; Wang and Francis, 2005). The gas can be produced by the increased corrosion of metallic wastes, drums, and/or containers, and organic waste degradation processes by microbial activities. The expected predominant gases are hydrogen (H_2), carbon dioxide (CO_2), and methane (CH_4) (Gillow and Francis, 2011; Small et al., 2008). In particular, low- and Intermediate-Level Wastes (LILWs) could be important for gas production because of

* Corresponding author at: Energy and Environment Directorate, Pacific Northwest National Laboratory (PNNL), 902 Battelle Blvd., P7-54, Richland, WA 99354, USA. Tel.: +1 509 372 6227; fax: +1 509 371 7344.

E-mail address: Wooyong.um@pnnl.gov (W. Um).

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the high proportion of organic elements that are biodegradable (Gillow and Francis, 2011).

More than 9,00,000 drums (200 L/drum) of LILWs were generated by Korean nuclear facilities, including 23 nuclear power plants, until 2012 (https://www.oecd-nea.org/rwm/profiles). A rock cavern type geological repository (i.e., silo disposal method) has been constructed at Gyeongju, Korea, to dispose of 1,00,000 LILW drums as a first stage of the waste disposal process (Fig. 1). According to the Korea Radioactive Waste Management Corporation (now, Korea Radioactive Waste Agency [KORAD]) (KRMC, 2008), approximately 84% of dry active wastes, which contained 69% of the LILWs generated by the nuclear facilities in Korea, consist of combustible wastes (mostly, organic materials) including rubber, cotton, wood, vinyl, plastic, paper, and activated carbon (Park et al., 2012). The performance of the Gyeongju LILW disposal facilities will be affected by microbial activities, because of the potential intrusion of groundwater to the repository after closure. Therefore, investigations of the biogeochemical effects must be conducted under in situ conditions to evaluate the safety of the Gyeongju repository performance.

Large-scale in situ experiments are under way using simulated LILW package drums placed in a basic disposal concrete container at the Gyeongju repository (Fig. 1). The experimental setup was benchmarked by Finnish experiments because their disposal method is similar to the Korean method (Park et al., 2010). The goal of this study, in part, is to determine the biogeochemical changes brought about by the activities of microorganisms at a comparatively early period after closure of the repository.

2. Materials and methods

2.1. Large-scale in situ experiments

The study area is at the Gyeongju geological repository site in the coastal area of southeastern Korea (Fig. 1), where the bedrock consists of mainly the Cretaceous granite (Choi et al., 2008). Clays (i.e., montmorillonite, zeolite, chlorite, and illite) are frequently observed as secondary minerals in the fractured zone, but not for calcite, and pyrite is widely scattered throughout local geology (Choi et al., 2008).

A large-scale concrete container was installed in the cavern 130 m below sea level in the Gyeongju geological repository. Nine 320-L steel drums were prepared by repackaging 200-L drums compressed under super-high pressure (Park et al., 2012), and were placed in the concrete container (collectively called a 9-Pack). Organic wastes such as vinyl, plastic, and cotton were included in the 320-L drums of the 9-Pack (Fig. 1). Groundwater collected from the Gyeongju geological repository was used to fill the 9-Pack to simulate the saturated environments expected in the LILW repository after its closure.

Two-liter sterile polypropylene containers were used to collect the groundwater, and water samples from the 9-Pack for geochemical and microbial analyses. The groundwater was overfilled into a sampling container, and then it was immediately sealed by a screw cap without headspace to minimize air contact with the water during sampling procedures. Geochemical and microbiological properties in the groundwater were investigated. After the large-scale in situ experiment began, the 9-Pack water samples, which were collected at 7, 21, and 35 days, were used for assessment of geochemical alteration. The types of microorganisms in the 9-Pack water samples collected at 7 and 63 days were determined in order to compare them with the microbes found in the initial groundwater sample. All the water samples including the groundwater sample were stored at 4 °C before the analyses. The generated gases were collected into the Tedlar® gas sampling bags of the online system installed on the 9-Pack container during 63 days.

2.2. Geochemical analyses

Water-quality parameters such as pH, oxidation reduction potential (ORP), dissolved oxygen (DO), and electrical conductivity were measured using multi-probes (Orion 5-Star™ meters; Thermo Scientific Co.). All water samples were filtered using a 0.45-μm polyvinylidene fluoride (PVDF) syringe filter before the chemical analyses. The concentration of anions (F^-, Br^-, Cl^-, NO_3^-, SO_4^{2-}, and PO_4^{3-}) was analyzed using a DX-60 Ion Chromatograph with

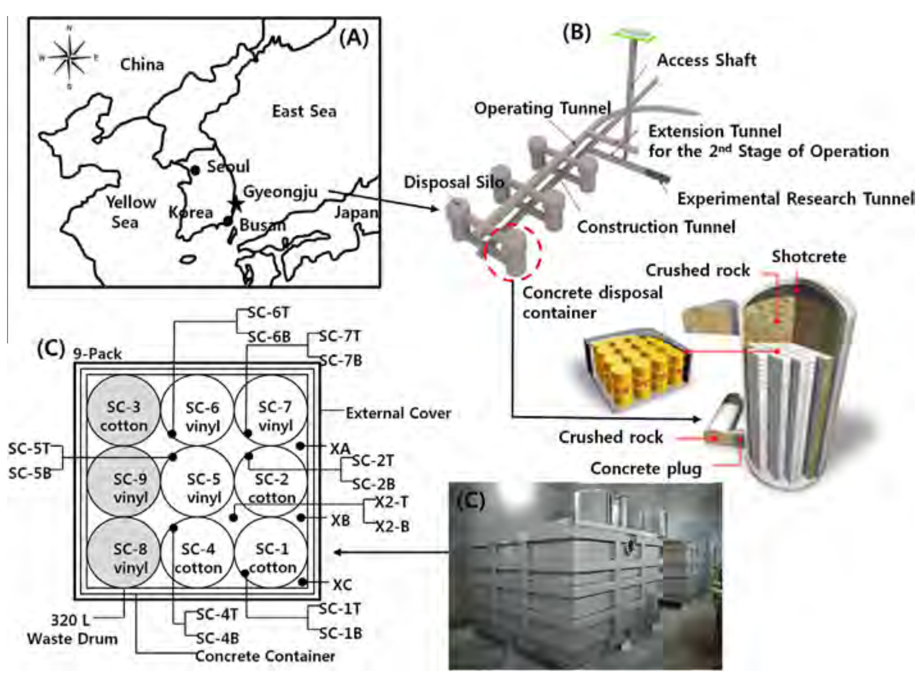

Fig. 1. (A) Location of the LILW disposal site in Korea, (B) schematic layout of disposal silos and unit concrete container and (C) experimental setup (9-Pack) for this study. In the layout of the 9-Pack, the solid points indicate individual sampling locations with sample name and position (top [T] or bottom [B]). The grey-colored waste drums were not used for sampling procedures.

an AS-21 column (DIONEX, USA). The cation concentrations (K^+, Na^+, Ca^{2+}, Mg^{2+}, and Fe_{Tot}) were determined using Inductively Coupled Plasma-Optical Emission Spectroscopy (JY Ultima2C, HORIVA Jobin Yvon Inc.). The water samples for cation analysis were treated with nitric acid before analysis to prevent any inorganic precipitation.

Total organic carbon (TOC) was analyzed using a TOC-VCPH analyzer (Shimadzu, Japan) after the water samples were filtered through a 0.22-μm PVDF filter. Volatile Fatty Acids (VFA) such as succinate, acetate, lactate, formate, propanoic acid, and ethanol were analyzed using high performance liquid chromatography mass spectroscopy (Agilent 1100 Series) with a Refractive Index Detector. The flow rate of 4-mM H_2SO_4 eluent was adjusted to 0.6 mL/min.

2.3. Microbial analyses

The standard Plate Count (SPC) was used for bacterial enumeration. The SPC microorganisms were enumerated by filtering the water samples through a sterile 0.22-μm membrane filter. The filter was placed on agar composed of 8 g L^{-1} Difco™ Nutrient Broth and 15 g L^{-1} Bacto™ Agar (BD), and incubated aerobically at 37 °C. The colonies were counted after 3–5 days of incubation using a binocular dissecting microscope (Microscopy Eclipse 80i, Nikon).

The SPC was conducted in the same manner as described above to determine the numbers of viable anaerobic or facultative anaerobic bacteria in the water samples. However, handling of water samples and plating was performed in anaerobic chamber (Bactron™, SC) saturated with mixed gases (N_2 90%, H_2 5%, and CO_2 5%). To the agar medium, 0.5 g L^{-1} of L-cysteine hydrochloride (Sigma–Aldrich) was added and the plates were anaerobically incubated until the colony numbers formed on each plate were constant.

To identify the bacteria, a single colony of SPC bacteria was selected by picking it from a membrane filter, and it was aerobically or anaerobically incubated at 37 °C for 3–5 days in a liquid medium. gDNA was isolated from the cultured microorganisms using a MagDEA DNA 200 Magtration System/12GC according to the manufacturer's (Precision System Sciences Co.) supplied protocol. Amplification and sequencing procedures for the isolated gDNA were performed at SolGent Co. (http://www.solgent.com). Briefly, the gDNA was amplified by PCR using universal primers 27F (AGAGTTTGATCMTGGCTCAG) and 1492R (GGYTACCTTGTTACGACTT) for bacteria (Suzuki and Gioannoni, 1996). BigDye terminator v3.1 Cycle Sequencing Kits (Applied Biosystems) were used for sequencing reactions. All cycling reactions were conducted by the Veriti 96-Well Thermal Cycler protocol programmed to initial denaturation at 96 °C for 1 min, and then 25 cycles at 96 °C for 10 s, 50 °C for 5 s, and 60 °C for 4 min. After excess dye terminators were removed by ethanol precipitation, PCR products were sequenced using an Applied Biosystems sequencer (ABI 3730XL DNA analyzer).

3. Results and discussion

3.1. Geochemical analyses

The groundwater used for saturation of the 9-Pack was neutral and suboxic with low total dissolved solids showing pH = 7.29,

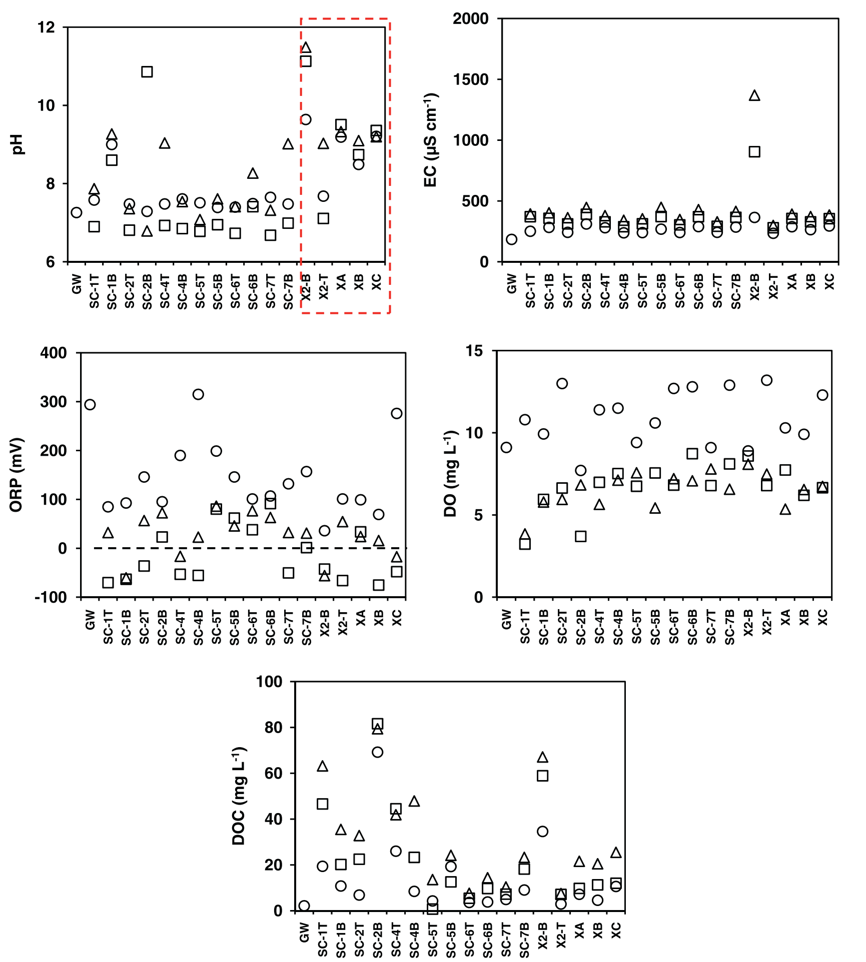

Fig. 2. The measured geochemical parameters for initial groundwater and water samples collected at each sampling location after 7 (○), 21 (□), and 35 days (△). Dashed boxes indicate the water sampled outside of the waste drums in the 9-Pack.

EC = 184 μS cm^{-1}, ORP = 294 mV, and DO = 9.11 mg L^{-1} (Fig. 2). Sodium was the dominant cation in the groundwater; the anions were bicarbonate, sulfate, and chloride (Fig. 3). The abundance of sodium, chloride, and sulfate in the groundwater could be influenced by the effects of seawater and pyrite oxidation in the study area. Seawater intrusion was supported by the positive correlation between sodium and chloride found in a previous study (Choi et al., 2008).

The measured geochemical parameters of water samples from the 9-Pack indicated that the environment of the waste unit container gradually changed to alkaline and more reducing conditions with increased reaction time. The pH and EC values increased, while the ORP and DO declined during the experiment compared to the initial groundwater sample (Fig. 2). The water samples evolved to (Na + K, HCO_3) type in the 9-Pack (Fig. 3). The increase in sodium and/or potassium reflected the leaching of salts from the concrete container and waste drums through cation exchange reaction. In particular, the water samples collected outside of the waste drums in the 9-Pack exhibited more distinct alteration in water type than water from within the waste drums. Higher pH values ranging from 9.03 to 11.5 were also observed in the outside samples after 35 days. These results suggest that the concrete material could play an important role in controlling the geochemical environment after the closure of the geological repository, because cementitious material contains alkalis and exhibits high pH (up to 12) levels in cement pores (Richardson and Taylor, 2013).

The 9-Pack waters showed a steady increase of DOC concentrations during the experimental period (Fig. 2). The greatest DOC concentration was approximately 80 mg L^{-1}, while the initial groundwater sample concentration was only 2.2 mg L^{-1}. The organic carbon was derived from the organic wastes such as cotton clothing, slippers, socks, gloves, plastic bags, vinyl sheets, and shoe covers that consist of biodegradable substances. After 35 days, the concentrations of DOC were greater for the waters sampled from the cotton-waste drums (i.e., SC-1, SC-2, SC-4) than from the other water samples. These results suggest that cotton materials may be more rapidly biodegraded than vinyl and plastics in the wastes.

3.2. Microbial activities and gas generation

The bacterial populations numerated were about ~10^2 CFU/100 mL in the initial groundwater sample under both aerobic and anaerobic conditions (Fig. 4). The microbial populations increased slightly after a 7-day reaction in the 9-Pack samples compared to the initial groundwater sample. The numbers of both aerobic and anaerobic microbes showed an increase up to approximately >8 orders of magnitude greater than the bacterial populations in the groundwater after the 35-day reaction, and they declined sharply between 35 and 63 days.

These microbial activities were strongly related to the decrease of DO and ORP at the early stage (~21 days after reactions) (Fig. 5), because the principal pathway of the microbial metabolism is an aerobic respiration for oxidation of organic carbon in the 9-Pack. The aerobic respiration is an energetically favorable reaction for bacterial growth (Maier et al., 2009; Wang and Francis, 2005). The DO is depleted as a result of the use of the electron acceptor associated with microbial growth and, consequently, the redox potential decreases to a reducing condition (Zehnder and Stumm, 1988). Aerobic bacteria may play a more important role than anaerobes during the very early period (<~35 days) in the 9-Pack until the oxygen source is completely consumed. In addition, facultative anaerobes could be activated with aerobic microorganisms during the early period, because the populations of both aerobic and anaerobic microbes decreased after 35 days.

Although post-35-day results for the geochemical parameters and specific identification of the microorganisms for the 9-Pack water samples were not available in this study, approximately 50 mg L^{-1} of ethanol was detected in the 9-Pack water sample after 63 days. The increased ethanol concentration supported the activities of anaerobic microorganisms through anaerobic metabolism

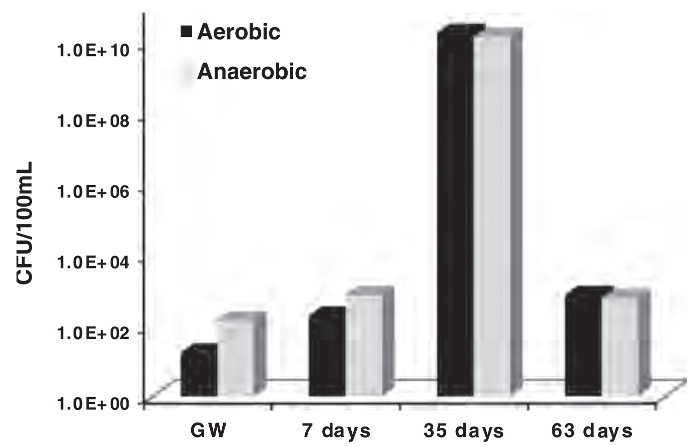

Fig. 4. Microbial populations in the initial groundwater and 9-Pack water samples.

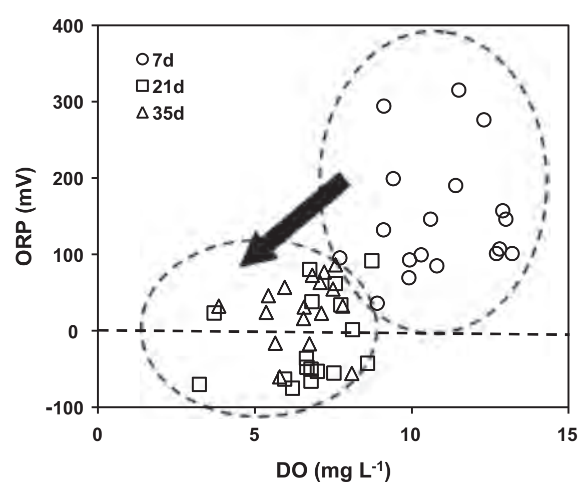

Fig. 5. Relationship between DO and ORP in the 9-Pack water samples during 35 days.

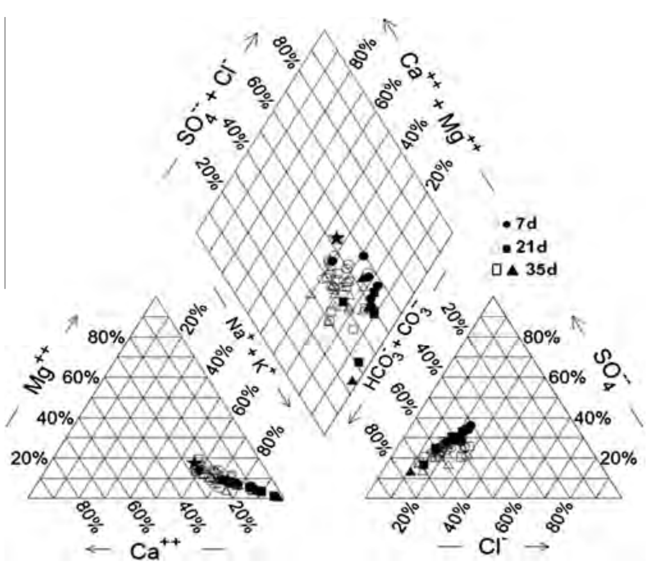

Fig. 3. Piper diagram for groundwater (★), and water samples collected outside (solid) and inside (open) of waste drums in the 9-Pack.

(Maier et al., 2009). The activities of aerobes and/or facultative anaerobes were activated between 7 and 21 days and slowed after 35 days, while the activities of anaerobic bacteria were considered to increase between 35 and 63 days. We postulate that the experimental duration of 35–63 days seems to be "transition period" from the proliferation of aerobes (or facultative anaerobes) to the growth of anaerobic microorganisms. However, during this study no detectable gases were found due to a short reaction time of 63 days.

4. Concluding remarks

The oxygen content seems to be the most important factor that will control the geochemical conditions and bacterial activities during the early stage after closure of the saturated LILW geological repository in Korea. Oxygen could be supplied to the repository system air trapped in the pores of the buffer materials, in backfill voids, in pockets of the surrounding rock, and as dissolved oxygen in the local groundwater (Pedersen, 1999). Microbial activities significantly accelerate the consumption of oxygen more than other geochemical reactions such as pyrite oxidation and ferrous iron dissolution (Wersin et al., 1994; Yang et al., 2007). For example, the activities of microorganisms depleted the oxygen within 1 month, but geochemical reaction took ~300 years to deplete the oxygen in the previous simulation (Yang et al., 2007). Although the redox potential exhibited a suboxic condition after 35 days in this study, over the long term the environment in the Gyeongju LILW geological repository is expected to exhibit a reducing condition based on the observed microbial activities.

Gases such as hydrogen and carbon dioxide were not observed in the 9-Pack throughout the 63-day incubation period. These results suggest that the experimental time of ~63 days may be insufficient to evaluate the impact of gas generation in the geological repository. Previous gas-generation study showed little gas evolution during the first year using similar large-scale experimental settings (Small et al., 2008). Although this study will continue for the next several years to evaluate the long-term safety of the Korean repository performance, the information derived from the early biogeochemical alteration can provide helpful information to establish the long-term stability and mobility of radionuclides and develop a remedial strategy against the release of radionuclides through unpredictable accidents and natural hazards right after closure of the geological repository.

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