Effect of Temperature on the Interaction of Nuclide With Metal Corrosion Products Under Anaerobic Alkaline Conditions

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1. Introduction

High-level radioactive wastes should be considered to be safely disposed with a metal disposal container in a deep underground site to isolate them from ecosystems. Generally, the materials of disposal containers are composed of iron (Fe) and copper (Cu) so that they can maintain geochemical stability. However, corrosion of the disposal canisters can occur due to oxidation-reduction changes, activity of microbes, and radiation effects. When the canisters are corroded, there may form chalcocite (Cu_2S), chalcopyrite ($CuFeS_2$) and mackinawite (FeS) as corrosion products [1]. These corrosion products may affect the chemical behavior of radionuclides that are leaching through them.

In this study, we investigated the effects of high temperature on the interaction between metal corrosion products and nuclides under anaerobic alkaline environment.

2. Materials and Methods

2.1 Heating Treatment of Metal Corrosion Products

Reagents of FeS and Cu_2S used in this study are purchased from Sigma-Aldrich.

The corrosion products are heated at high temperature to later investigate the temperature effects on the interaction between metal corrosion products and nuclides. Both solids of FeS and Cu_2S were heated with dry or wet state in aerobic conditions. In a case of dry-heating, 10 g of each corrosion product was placed in 125 ml-FED bottles and heated to 150°C for 5 days. In a case of wet-heating, H_2O_2 was used as an oxidizing agent and it was added with 0.35 ppm in a 125 ml-serum bottle containing the solids. The bottle was heat-treated at 90°C for 5 days. Finally, the supernatant was removed after centrifugation (5,000 rpm, 5 minutes) and the precipitated solids were freeze-dried.

2.2 Sorption of Nuclides

To investigate the sorption of nuclides on the corrosion products, raw and (dry and wet) heat-treated solids of FeS and Cu_2S were prepared. Three types of those solids were added to each 125 ml-serum bottles in an amount of 100 mg. 100 ml of distilled water was added to the bottles, and they were purged with N_2 gas for 40 minutes to remove oxygen in the solution. Cesium (Cs) and iodine (I) were selected as main nuclides, and they were injected to the solution to be 10 ppm. To know the sorption amount of the nuclides under alkaline conditions, 1.0 N NaOH solution was used to adjust the media as pH 7, 9, and 11. The solution was placed in an incubator shaker for 24 hours (100 rpm at 30°C). During the reaction, the supernatant was sampled after 1, 2, 4, and 24 hours and analyzed by ICP-MS to determine the sorption concentrations of the nuclides and dissolution of metal corrosion products over time. After the experiment, the solid samples were obtained from the centrifugation (5,000 rpm and 5 minutes) and freeze-dried. They were investigated by SEM-EDS to analyze nuclide sorption characteristics.

3. Results and Discussion

The wet-heated FeS sample became reddish unlike Cu_2S. It appears to have oxide-type secondary minerals that combined with the dissolved oxygen

present in the water.

Adsorption of iodine was observed in all types of Cu_2S, and it was significant at pH 7 (Fig. 1). At the same pH 7 condition, the iodine sorption gradually increased with time in the raw- and dry-heated solids of Cu_2S, but decreased for a wet-heated solid after 4 hours. It is presumed that iodine sorption on the oxidized solid is not strong. In addition, iodine was predominantly adsorbed onto the surface of Cu_2S rather than FeS.

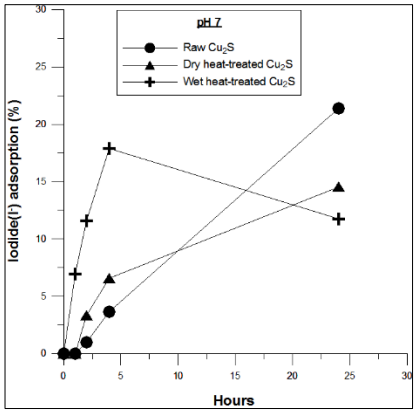

Fig. 1. Characteristic iodide adsorption curves by three solid types of Cu_2S at pH 7.

The FeS was highly sensitive to pH changes. The dissolution of FeS was active at neutral pH. However, at pH 11 the FeS dissolution became weak with increase of cesium sorption over time (Fig. 2).

By SEM-EDS, we confirmed nuclides such as iodine and cesium present on the surface of corrosion products (Cu_2S and FeS).

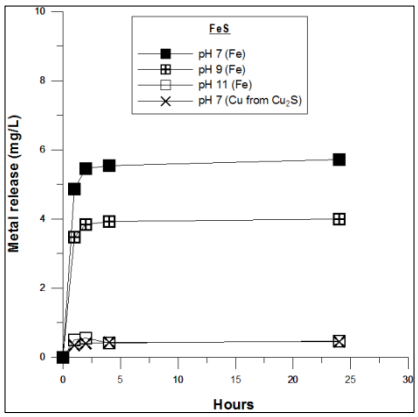

Fig. 2. Metal release from the corrosion products under various pHs.

4. Conclusion

The effect of high temperature on the interaction between corrosion products and nuclides was investigated under anaerobic alkaline conditions. It was found that the sorption of radionuclides was affected by heat-treated sample types and pHs. We confirmed that the change of corroded products by high temperature may delay or accelerate the migration of radionuclides in anaerobic disposal environments. Therefore, it is needed to further study the effect of high temperature on the sorption behaviors of radionuclides onto the metal corrosion products in anaerobic conditions.

ACKNOWLEDGEMENT

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REFERENCE

[1] J.K. Lee et al., Complex Behavior of Radionuclides in a Deep Geological Environment, KAERI/TR-6547/2016, 2016.