Sorption Characteristics of Iodide on Container Corrosion Products Under the Disposal Conditions: Case Study for Chalcocite and Mackinawite in Alkaline Conditions

Chung-Kyun Park*, Tae-Jin Park, Seung-Yup Lee, and Jae-Kwang Lee
Korea Atomic Energy Research Institute, 111, Daedeok-daero 989beon-gil, Yuseong-gu, Daejeon, Republic of Korea
*ckpark@kaeri.re.kr

1. Introduction

In terms of long-term safety for radioactive waste disposal, the anionic iodide (I-129) with a long half-life (1.6 X 10^6 yr) is of a critical importance because this radionuclide migrates in geological media without any interactions. Various studies have been performed to retard the iodide migration. Recently, some minerals that are likely generated from waste container corrosion, have been suggested to have a considerable chemical interaction with iodide. In this study, chalcocite (Cu_2S) and mackinawite (FeS) were selected for underground corrosion materials, and an iodide sorption experiment were carried out.

2. Sorption experiment

NaI was used as the iodide for the sorption. Chalcocite and mackinawite were used as sorption minerals. In the sorption test, 50 ml of the experimental solution was put into 1 g of the target mineral, and 0.01 M of sodium hydrosulfite ($Na_2S_2O_4$) was added to maintain the reducing conditions. The initial concentration of iodine is about 1 mM. In order to investigate the pH effect in the alkaline condition, the pH of the solution was divided into four different regions: 8.4, 10.3, 11.4 and 12.4. The NaOH was used to adjust the pH of the system. After the two weeks of the sorption reaction, the sample solution was centrifuged at 8600 rpm for 20 minutes and then filtered through a 0.2 μm filter. The minerals that reacted with iodide were separately collected and the amount of iodine was determined using the sequential chemical extractions with 0.1 M $CaCl_2$ and KCl on the minerals collected [1].

3. Results and Discussion

3.1 Iodide sorption onto the iron-copper-sulfur minerals as corrosion products

In general, the surface of the minerals are electrically negative, so the sorption is not expected for anions such as iodide. However, the sorption occurred at a considerable level for the two minerals tested. We note that this suggests an important reaction that prevents the notorious anion migration in a deep underground environment in the field of disposal safety. In Fig.1, the K_d calculated for I^- sorption onto the chalcocite was larger than that for the mackinawite. This likely indicates that the I^- substitution with OH^- on the Cu-minerals is much easier than that on the Fe-minerals and this behavior can be explained by the hard-soft acid-base theory [2]. In the theory, the hard molecules or ions possess a high electronegativity, high charge density, low polarity and low oxidative potential, and reacts better with the hard ones, whereas the soft ones react better with the soft ones. Thus, the iodide or sulfide as the weaker base reacts better with the cation, such as Cu^+, Hg^+, and Ag^+, as the weaker acid than the hydroxide, which is the harder base. The Fe^{2+} ions are relatively neutral, and thus their reactivity with iodide is relatively low and exhibits a low sorption ability.

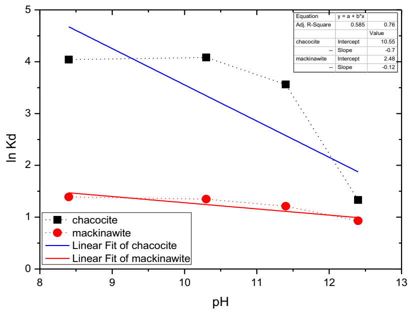

Fig. 1. Curve fittings of Kd for the iodide sorption onto chalcocite and mackinawite as a function of pH.

3.2 Competition between the iodide and chloride sorbed onto the minerals

Fig. 2 shows the amount of iodide extracted by chloride with respect to the pH and the iodide sorption ratios onto the minerals. For the chalcocite, about 80% of the iodide was desorbed under a pH of 11. This indicates that the chloride does not have an absolute advantage in the reaction with Cu over the iodide, because about 20% of the iodide is still bound to Cu, when the iodide is 100 times less than the chloride. On the other hand, about 70% of the iodide is still bound to Fe for the mackinawite. This indicates that the iodide sorbed onto the mackinawite surface forms even stronger bonds than the chalcocite, and it is harder to exchange the iodide with the chloride.

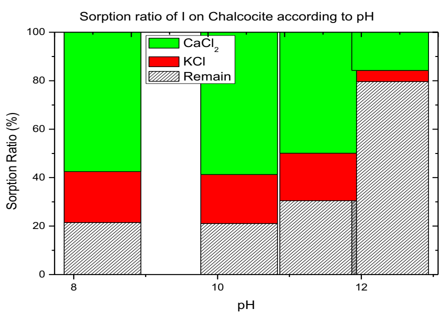

Fig. 2. Extracted iodide sorption ratios according to the pH.

4. Conclusion

Chalcocite exhibited better iodide sorption ability than mackinawite for most of the pH range, indicating that the softer iodide can react better with softer copper ions than with iron. When the pH was higher than 12, the iodide sorption ability decreased for both minerals, likely due to the competition with the hydroxides in the iodide sorption. Our results suggest that chalcocite and mackinawite, which can be the secondary minerals from corrosion, can retard the iodide migration under alkaline conditions with a pH value of less than 12.

ACKNOWLEDGEMENT

We acknowledge the Korean Government, Ministry of Science, ICT and Future Planning (MSIP), for support (No. 2017M2A8A5014859).

REFERENCES

[1] C.K.PARK, M.H.BAIK, and Y.K.KOH, " Diffusion and sorption properties of some sorbing nuclides onto granodiorite" , Nuclear Technology. 196, 121-129 (2016).

[2] R. Pearson, " hard and soft acids and bases – the evolution of a chemical concept" , Coordination chemistry reviews, 100, 403-425, (1990).