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Original Article

Sorption characteristics of iodide on chalcocite and mackinawite under pH variations in alkaline conditions

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ABSTRACT

In terms of long-term safety for radioactive waste disposal, the anionic iodide (I-129) with a long half-life (1.6 × 10^6 yr) is of a critical importance because this radionuclide migrates in geological media with limited 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 and mackinawite were selected as candidate minerals for underground corrosion materials, and an iodide sorption experiment were carried out. The experiment was performed under anoxic and alkaline conditions and the pH effects on the iodide sorption were investigated in the range of pH 8 to 12. The results showed that both minerals demonstrated a noticeable sorption capacity on iodide, and the distribution coefficient (K_d) decreased as the pH increased in the experimental condition. In addition, when the alkalinity increased higher than a pH of 12, the sorption capacity of both minerals decreased dramatically, likely due to the competition of hydroxy ions with the iodide. This result confirmed that chalcocite was an especially good sorbing media for iodide under alkaline conditions with a pH value of less than 12.

1. Introduction

In canisters of radioactive waste that are disposed of in the deep underground, the groundwater will, over time, penetrate into the disposal system, corrode the canister, and dissolve the waste, releasing radionuclides. Radionuclides will, at some point, gradually migrate to the biosphere along with the groundwater. Since this process takes a very long time, most of the radionuclides will either disappear as they decay or stop their migration into the biosphere due to the interaction with the underground media, including rocks and soil. Nevertheless, some of the most important radionuclides to be considered in disposal safety assessment are the anionic radionuclides, which have very long half-lives. They include I-129, Tc-99, and Se-79 with half-lives of 1.6 × 10^7, 2.1 × 10^5, and 6.5 × 10^4 years, respectively. Among them, I-129, which has the longest half-live, is the most noticeable anionic radionuclide for safety assessment, because it is among the first wave of nuclides entering the biosphere after disposal, and can be bioaccumulated in the thyroid when ingested. Iodide-129 is known to have almost no geochemical interactions with natural barriers (the underground media) or engineered barriers (canisters, buffers, etc.) in deep underground reducing conditions, and thus it can easily migrate into the biosphere along the groundwater pathways, regardless of the effect of physical delays, including diffusion and dispersion [1]. Anionic species of iodine and iodide are stable over a wide range of pH and Eh conditions in solution [2], while some of I^- can be oxidized biotically or abiotically under subsurface oxidizing and organic-rich environments, forming iodate and organic complexes. Those will interact with sediments and soils. Nevertheless, iodide has a significant potential of reaching surface biosphere before decaying to insignificant level. Thus, some solid media that can interact with these anionic radionuclides are of fundamental importance in research on the disposal of nuclear waste, and this includes the corrosion products from long-term evolution in the deep underground disposal environment [3]. It is known that iron, copper, and sulfur-related minerals, which are abundant and can be generated from canister corrosion in a disposal environment, are highly reactive with anionic radionuclides [4,5]. To clarify key issues regarding the long-term safety of radioactive waste disposal, it is necessary to understand the behavior of radionuclides, the interactions between radionuclides and the minerals of interest, and the long-term stability of the minerals under deep underground

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disposal conditions, which are dramatically different from aboveground conditions.

To secure a safe disposal of long half-life nuclides, it is important to bind nuclides in deep underground away from subsurface, eventhough iodine can be form iodate or per-iodate and sorb on soils and organics in aerobic subsurface environments [3,6]. Therefore, many efforts for developing robust canisters and backfill materials have been carried out. Iron or copper, which are the main elements of the many disposal canisters currently in the deep underground environment, may be corroded by the evolution of the redox conditions of the groundwater, the reaction with microorganisms, and the radiation from the radionuclides in the waste. Minerals including chalcocite (Cu_2S), chalcopyrite ($CuFeS_2$), mackinawite (FeS), and pyrite (FeS_2) can be generated as corrosion products on the surface of an iron canister or from copper when copper is used as coating materials for the canister. Through the breached hole of the canister, groundwater will reach and dissolve nuclides in the waste body slowly but steadily, and the released nuclides can migrate through groundwater and contact the corrosion products around containers and backfill materials. The behavior of the radionuclides and their interactions with these corrosion-originated minerals has recently received attention, but understanding of the behavior still lacks the fundamentals. Basley et al. [7] investigated iodide sorption on cinnabar and chalcocite in the range of pH 4 and pH 10, and concluded that iodide exchanged hydroxyls attached to Hg and Cu sites of the minerals. Lefevre et al. [8–10] studied sorption of iodide on cuprous sulfide minerals and identified the oxidized layer of the minerals with XPS in presence of air. Lee et al. [5] developed an iodide binding mechanism with a microbial copper reduction method to form a crystalline halide salt of CuI at near neutral pH and anaerobic conditions. Meanwhile, reactions to retard iodine migration using silver, which can form AgI as precipitates, have been relatively well studied [11–13], but it is generally accepted that the expensive silver is not economical for use in the disposal system.

Generally it is assumed that the high-level wastes would be disposed and located in a deep underground for a very long time. The environment of the deep underground is different from that of the ground, especially the redox condition is anoxic (i.e., lack of oxygen) and the pH condition is slightly alkaline. Moreover a concrete structure could be used as an engineering barrier, and it is a cause of increase of pH values of the groundwater around the disposal system. We investigated the interactions of iron-copper-sulfur minerals, which are the candidate corrosion products in the deep geological disposal environment, with the anionic radionuclide under anoxic and alkaline conditions. The sorption reactions of iodide were investigated on chalcocite (Cu_2S) and mackinawite (FeS) in a pH range of 8–12. We conducted this study to understand the behaviors of anionic radionuclides in the presence of corrosion products from the engineered-barrier system in the disposal environment and to provide a way to retard the critical anionic radionuclide migration to the biosphere.

2. Sorption experiment

Reagent-grade NaI (Sigma-Aldrich) was used as the iodide for the sorption. Three times deoxygenated distilled water was used to prepare the reagents. Chalcocite (Cu_2S, Aldrich) and mackinawite (FeS, Sigma-Aldrich) 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 min and then filtered through a 0.2 μm filter to remove the minerals and any possible precipitates. The initial and final pH was measured to compare the pH alteration during the sorption reactions. 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

The results of the sorption test are summarized in Table 1. The sorption distribution coefficients (K_d) for chalcocite and mackinawite are shown according to the pH values (pH of 8.4, 10.3, 11.4, 12.4). In general, the surface of the underground media and minerals are electrically negative, so the sorption onto the minerals of interest is not expected for anions such as iodide. However, as summarized in Table 1, 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. The results also revealed that there was a considerable difference in the sorption values between the two minerals (chalcocite and mackinawite), whereas the sorption tendency according to the pH followed a certain pattern for the two.

As shown in Table 1, the distribution coefficients (K_d) at a pH of 8.4, 10.3, 11.4, and 12.4 were 56.8, 58.9, 35.2, and 3.8 for the chalcocite, respectively, and 4.0, 3.9, 3.4, and 2.5 for the mackinawite, respectively. The K_d for the chalcocite was about ten times larger than that for the mackinawite at a pH of 8.4, 10.3 and 11.4. This is likely due to the differences in the chemical reactivity among iodine, copper and iron. According to the hard-soft acid-base theory [15], copper is softer than iron, and thus more reactive with iodine when iodine is considered soft. Moreover, the solubility of the minerals and the oxide formation on the mineral surface in water may be additional factor to make the difference in the K_d between the minerals. When an oxide layer is formed on the surface of these minerals, the number of iodide ion sorption sites decreases. In general, iron sulfides or copper sulfides interact easily with oxygen. Therefore, it is easy to see $FeSO_4$ and $CuSO_4$ layers are formed by the oxidation of commercial iron or copper sulfides [8,16]. Although, the mineral surface analysis was not performed separately in this experiment, we needed to consider the formation of the oxide layers (e.g., $FeSO_4$ and $CuSO_4$) on even the sealed reagent grade chemicals and its influence on the iodine sorption test.

The equilibrium constant for the chalcocite ($K_{sp} = [Cu^+]^2[S^{2-}]$) was 10^{-48}, which is regarded as extremely low, whereas that for the mackinawite ($K_{sp} = [Fe^{2+}][S^{2-}]$) was 2.3×10^{-4} to 1.6×10^{-19} [7,17]. Mackinawite is more soluble and more reactive with the oxygen in water than chalcocite, and thus the oxide layers on the mackinawite surface are expected to form better. In addition, some of the $FeSO_4$ and $CuSO_4$ oxide layers are dissolved in water to form SO_4^{2-}, and thus they compete with iodide in terms of iodine sorption onto the minerals [6]. The mackinawite in this system should create more interference in the sorption from the sulfate ions than the chalcocite. To exclude influence of the oxidation layers, Lefevre et al., used a synthetic chalcocite for iodide sorption reactions, and this resulted in a K_d value of 2440 ml/g at a pH of 8.5 [8]. The main objective of my test is not investigating the surface phenomena of the pure minerals, but evaluating sorption ability of the minerals on iodide under underground disposal environments. As a result, K_d

Table 1
Distribution coefficients on chalcocite and mackinawite according to pH unit: [ml/g].

pH	Chalcocite (Cu_2S)		Mackinawite (FeS)	
	K_d (in this work)	K_d [reference value]	K_d (in this work)	K_d [reference value]
8.4	57	2440 [8], 600 [7]	4.0	0.17 [14]
10.3	59	50 [7]	3.9	
11.4	35		3.4	
12.4	3.8		2.5	

was calculated as 57 ml/g at a pH of 8.4 in this study, which shows a noticeably large difference from the K_d value obtained from Lefevre's work. This indicates that the formation of oxide layers on the chalcocite surface dramatically influences the iodide sorption reactions by the interferences described above. On the other hand, Basley et al. [7] performed a sorption test for iodide to reflect the cementitious repository environment. The results showed 58% and 97% increases in K_d values under $CaSO_4$ saturated conditions as compared with those under the SO_4 absent conditions at a pH of 8 on chalcocite and cinnabar, respectively. In our work, we have not used $CaSO_4$ in the sorption test and thus, we think our K_d value of 57 ml/g at the pH of about 8 can similarly be increased at the $CaSO_4$ saturated condition.

3.2. *Sorption mechanism and the pH effect*

In our sorption test, the distribution coefficient roughly decreases with an increasing pH for both minerals (Table 1). It is understood that as the pH increases, the number of OH^- ions increase in the solution, and thus the K_d decreases due to the competition of OH^- and I^- ions for the sorption onto the minerals. According to Elprince et al., the surface charge of minerals can be distinguished by the pH-dependent and isomorphically-substituted surface charge density [18]. This surface charge, which can determine the electronic potential, can be neutralized by the diffusion layers of the electronically opposite charges and fixed to the hydrogen ions. These fixed and diffused charges form electrical double layers. Thus, the surface charges can be expressed as a function of the pH, and the sorption onto the mineral surface possesses a thermodynamic functional relationship. When an ion exchange reaction is the main sorption mechanism, it follows linear relationship below:

$$\ln K_d = a + b * pH$$

Where *a* and *b* are constants originated from the derived thermodynamic functions to define the experimental conditions [18,19]. From this equation, we obtained the curve fittings for the $\ln K_d$ as a function of the pH by inserting our experimental data in Table 1. The fittings are shown in Fig. 1 and their slopes, intercepts and errors are summarized into Table 2. The obtained *a* and *b* values are 10.55 ± 3.00 and −0.70 ± 0.27 for chalcocite, respectively, whereas 2.48 ± 0.35 and −0.12 ± 0.03 for the mackinawite, respectively. As for chalcocite, the linear slope is not fitted well to the experimental data and the error is larger than that for mackinawite. This indicates that chalcocite has a significant alteration upon the pH variation compared with mackinawite in the iodide sorption. There is a small variation in the pH between 8.4 and 11.4, but a rapid change in the pH over the 12 region, which suggests a large change in the sorption mechanism over the pH of 11.5. The concentration of the iodide in this experiment is about 10^{-3} M. When pH is less than 10, the concentration of $[OH^-]$ is less than 10^{-4} M and $[I^-]$ is dominant in the solution. At pH is 11, the concentration of $[OH^-]$ is 10^{-3} M and compete against iodide in the solution. However, when pH is over 12, the concentration of $[OH^-]$ is over 10^{-2} M, so $[OH^-]$ is predominant in the solution. Thus, the sorption of iodide decreases sharply at a pH 12 or higher.

The distribution coefficient obtained from the batch test is a measure of the apparent amount of the sorption, but it is the result of various reactions between radionuclides and the mineral surfaces, including physicochemical adsorption, surface precipitation, and bonding with the mineral structures. Physical adsorption involves the van der Waals attraction or the electrostatic complex formation to form an outer sphere complex by the ion exchange, whereas the chemical bonding forms an inner sphere complexation by the ligand exchange, covalent bonding, and chemisorption. The former is reversible, whereas the latter is in general highly irreversible. We focused mainly on the chemical reactions between the mineral surface structures and the iodide to understand in detail what reactions occur.

Fig. 2 illustrates the surface bonding type of the minerals according to the pH. For the case of mackinawite, the point of zero charges (pH_{PZC}) is checked at 7.5 by acid-base titrations [21]. When the pH is higher than the pH_{PZC}, the OH^- ions increase their numbers in water and H^+ ions release from the thiol group on the mineral surface. This can be expressed as the following chemical formula:

$$=M - SH \leftrightarrow\ = M\text{-}S^- + H^+$$

$$H^+ + OH^- \leftrightarrow H_2O$$

Where = M represents Cu or Fe as the metals in the mineral structure. A higher pH in the solution makes more negativity on the surface of minerals, and the iodide as an anion becomes more resistant to reaching the mineral surface. Thus, the sorption of the iodide onto the minerals at a pH of 12 or higher decreases sharply. This tendency was more noticeable for the chalcocite than for the mackinawite. Additionally, it is known that not only are the hydrogen ions released from the thiol group, but also the sulfur ion itself can be released from the metal. Then the vacancy formed on the mineral surface can be filled with the abundant hydroxyl group in alkaline conditions, and the surface of the minerals becomes hydrated as Fe-OH and Cu-OH . Thus, the iodide can substitute for the hydroxide on the mineral surface and finally it results in the Cu-I or Fe-I [7]. This can be expressed as follows:

$=M\text{-}S_n + mOH^- \leftrightarrow\ = M\text{-}(OH)_m + nS^{2-}$, where $n = 2$ m, an arbitrary number

$$=M\text{-}(OH)_n + nI^- \leftrightarrow\ = M\text{-}(I)_n + nOH^-$$

In our work, the K_d calculated for I^- sorption onto the chalcocite (Cu_2S) was larger than that for the mackinawite (FeS). 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 [15]. In the theory, the hard molecules or ions possess a high electronegativity, high charge density, low polarity and low oxidative potential, and reacts better

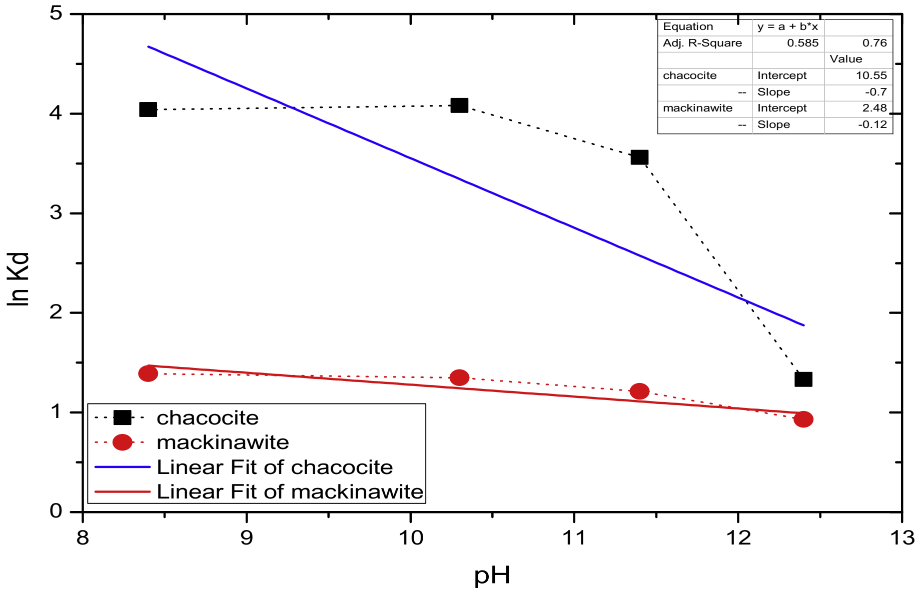

Fig. 1. Curve fittings of K_d for the iodide sorption onto chalcocite and mackinawite as a function of pH.

Table 2
Parameter values of the curve fitting on chalcocite and mackinawite.

Mineral	slope error	intercept error
chalcocite	- 0.70 0.27	10.55 3.00
mackinawite	- 0.12 0.03	2.48 0.35

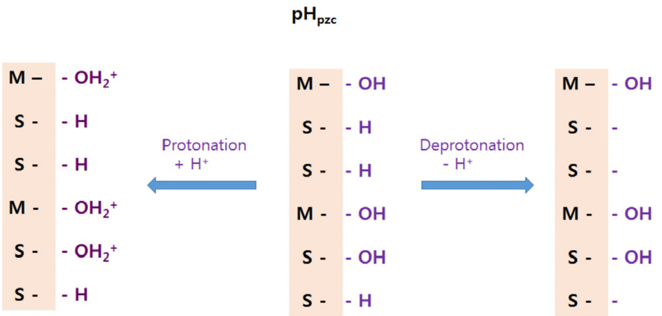

Fig. 2. A schematic illustration of the functional groups on the mineral surface according to pH (modified from ref. [17] & [20]).

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.

3.3. *Competition between the iodide and chloride sorbed onto the minerals*

$CaCl_2$ and KCl are easily dissolved in water, so Cl^- ions are abundant in groundwater. Similar to I^-, Cl^- reacts well with the minerals. Thus, once the iodide is sorbed onto the minerals, there is a potential for the iodide to be exchanged with the chloride in the disposal environment. To investigate the competition between the I^- and Cl^- with the mineral in an aqueous solution, we used 0.1 M of chloride, which is 100 times in excess of the iodide concentration, to extract the iodide adsorbed onto the mineral surfaces. Representative substitution reactions are expressed as

$$=\text{M-I}^{-}+\text{Cl}^{-} \rightarrow =\text{M-Cl}^{-} + \text{I}^{-}$$

Where, $=$M represents Cu and Fe as the metal atoms on the mineral structure.

Table 3 and Fig. 3 show 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 up to a pH of about 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. This suggests that the absolute amount of the K_d value for iodide sorption is larger for chalcocite than for mackinawite, whereas the stability of the iodide-sorbed mineral for the makinawite is higher than that for the chalcocite. At higher pH conditions (i.e., pH of 12.4), the iodide remains about 80% for both the chalcocite and the mackinawite, suggesting that the OH ions play an important role in the competition in exchanges for anion sites. The concentration of chloride in this experiment is about 10^{-1} M. When pH is over 12, the concentration of $[OH^-]$ is over 10^{-2} M, so $[OH^-]$ competes with $[Cl^-]$ to exchange the sorbed iodine on the mineral surface. Moreover anion exclusion from deprotonated mineral surface also strongly depress approaching of $[Cl^-]$ at high pH value.

The competitive interactions of the anions, such as Cl^-, I^-, Br^-, and F^-, are an important issue when we consider a real underground environment. In this work, we carried out the chemical extraction with chloride for iodide to check their sorption reversibility of iodide. We used one hundred times excess chloride and the results showed the chloride could replace the sorbed iodide at the pH range of 8–11. In a real groundwater, there are so many anionic components including not only simple ions such as Br^-, F^-, and Cl^-, but also anionic complexes such as carbonates, sulfide, colloids, and so on. In principle, they also compete for sorbing on

Table 3
Amounts of iodide extracted according to pH.

pH	Chalcocite				Mackinawite			
	Total	$CaCl_2$	KCl	remain	Total	$CaCl_2$	KCl	remain
	amounts, mg/g (ratios, %)	amounts, mg/g (ratios, %)	amounts, mg/g (ratios, %)	amounts, mg/g (ratios, %)	amounts, mg/g (ratios, %)	amounts, mg/g (ratios, %)	amounts, mg/g (ratios, %)	amounts, mg/g (ratios, %)
8.4	1.13 (100.0)	0.65 (57.5)	0.24 (21.0)	0.24 (21.5)	0.157 (100.0)	0.050 (31.7)	0.002 (1.0)	0.106 (67.3)
10.3	1.15 (100.0)	0.67 (58.7)	0.23 (20.3)	0.24 (21.0)	0.152 (100.0)	0.030 (21.6)	0.001 (0.6)	0.118 (77.8)
11.4	0.88 (100.0)	0.44 (49.9)	0.17 (19.6)	0.27 (30.5)	0.134 (100.0)	0.026 (19.8)	0.002 (1.5)	0.105 (78.7)
12.4	0.15 (100.0)	0.02 (15.7)	0.01 (4.6)	0.12 (79.6)	0.015 (100.0)	0.015 (14.6)	<0.001 (0.2)	0.087 (85.2)

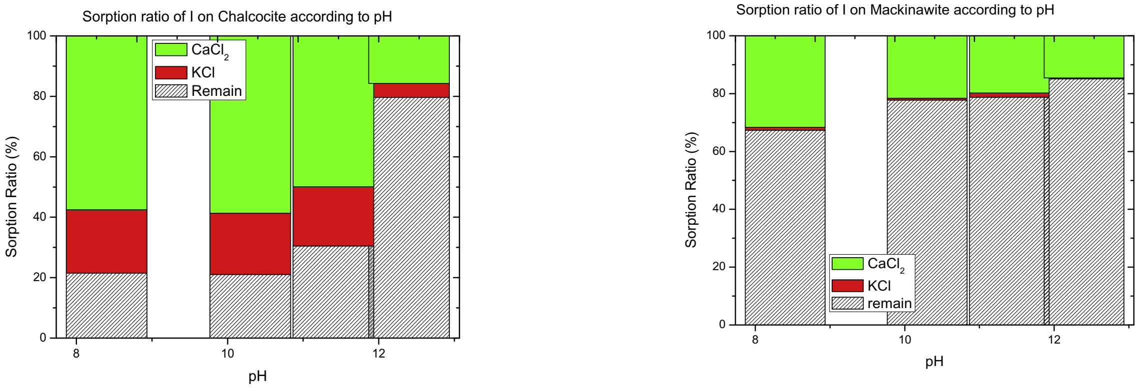

Fig. 3. Extracted iodide sorption ratios according to the pH.

the minerals against iodide. However, the concentrations of the bromide, fluoride, and many others are much lower than that of iodide and chloride in a real system. We think the effect of the bromide or fluoride in the competitive sorption against iodide will be negligible, especially when we consider them in the safety assessment for the disposal system. In addition, the chemistry between the stable iodide and I-129 in groundwater or in the radioactive wastes is identical, so the effect from it depends upon the ratio between the iodides and the sorbing materials from the disposal research perspective. Therefore, to apply the K_d data for iodide in a safety assessment, specific consideration is recommended on the geochemical aspects of the disposal environments.

4. Conclusion

We conducted iodide sorption experiments with iodide as a representative anionic radionuclide for chalcocite and mackinawite, which are the minerals that can be generated by corrosion from the waste canisters under deep geological conditions. The pH conditions ranged from pH 8 to 12, because the disposal condition is a reduced alkaline environment. 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. Once the iodide sorbed onto the minerals, makinawite demonstrated better stability than chalcocite in the extraction by the chloride ions. 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.

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