Sorption of I and Se onto Green Rusts with Different Interlayer Anions, GR(CO$_3^{2-}$) AND GR(Cl$^-$)

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Abstract : *Natural green rust (GR) can retard the migration of anions through geological media because it has a Layer Double Hydroxyl (LDH) structure with a positive charge. In this study, the sorption behaviors of anions such as selenite (Se(IV)O$_3^{2-}$), selenate (Se(VI)O$_4^{2-}$), and iodide (I$^-$) onto green rusts with different structures, i.e., GR(Cl$^-$) and GR(CO$_3^{2-}$), were investigated by conducting batch sorption experiments in an anoxic condition. Experimental results showed that selenite was mostly sorbed onto GR(CO$_3^{2-}$) and then partly reduced to metal selenium, Se(0). However, little selenate and iodide was sorbed onto GR(CO$_3^{2-}$) while some iodide was sorbed onto GR(Cl$^-$). It is presumed from the experimental results that the major sorption mechanism of SeO$_3^{2-}$ and I$^-$ onto green rusts is the anion exchange reaction with the anions existing in the interlayer of the rusts. Green rust, therefore, can play an important role in the retardation of anions migrating through deep geological environments owing to its LDH structure with a high anion exchange capacity.*

Keywords : *Green rust, Selenium, Iodide, Anion exchange, Sorption, Reduction*

1. INTRODUCTION

In a proposed geological disposal system for high-level radioactive waste in Korea, metal canisters and compacted bentonite clay have been considered as engineered barriers [1]. Based on the Korean disposal concept, a metal canister containing high-level radioactive waste is installed into a compacted bentonite buffer emplaced in disposal boreholes located in a deep underground repository. The proposed metal canister is made of iron, and its exterior is coated with a corrosion-resistant copper metal [1]. In deep geological conditions for the disposal of high-level radioactive wastes, the iron canister will corrode into green rust (GR) [2-4]. The dissolution of Fe(II) on the surface of the iron canisters will proceed to corrosion of the iron canisters as follows: Fe(II) → Fe(II)(OH)$_2$ and/or Fe(III)(OH)$_3$ → green rust(GR) → lepidocrocite or magnetite → goethite or hematite etc. [5-7].

GR is a natural corrosion product of stainless steel and iron that can be formed in compacted bentonite and rein-forced concrete [8, 9], in seawater [10, 11], and in water supply pipes [12]. GR is known to exist in a stable state when the environment is near a transition zone between Fe(II) and Fe(III) or between the oxidized and reduced layers of underground environments. GR is thus considered one of the major corrosion products of iron canisters in deep geological conditions for radioactive waste disposal [3, 4, 13].

Radionuclides such as selenium, iodine, and technetium present as anions in geological environments are of great concern in the context of radioactive waste disposal because of their limited sorption onto geologic materials [14]. In particular, selenium exists in various chemical species with different oxidation states such as Se(-II), Se(0), Se(IV), and Se(VI) under most geochemical conditions (see Fig. 1). Iodine usually exists as iodide (I$^-$) under most geochemical conditions [15].

GR composed of a mixture of Fe(II) and Fe(III) is a very sensitive iron oxide with respect to oxidation and a very strong reducing agent. In particular, surface-bound Fe(II) species have been reported to have a stronger reducing potential than Fe(II) species dissolved in a solution[5]. The formation of GR depends upon the Fe(II)/Fe(III) ratio and pH, and the former ranges between 1 and 4.5 [16]. The chemical formula of GR is generally given as [17, 18] :
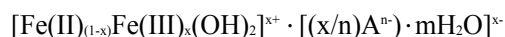
$$[\text{Fe(II)}_{(1-x)}\text{Fe(III)}_x(\text{OH})_2]^{x+} \cdot [(x/n)\text{A}^{n-}) \cdot m\text{H}_2\text{O}]^{x-}$$
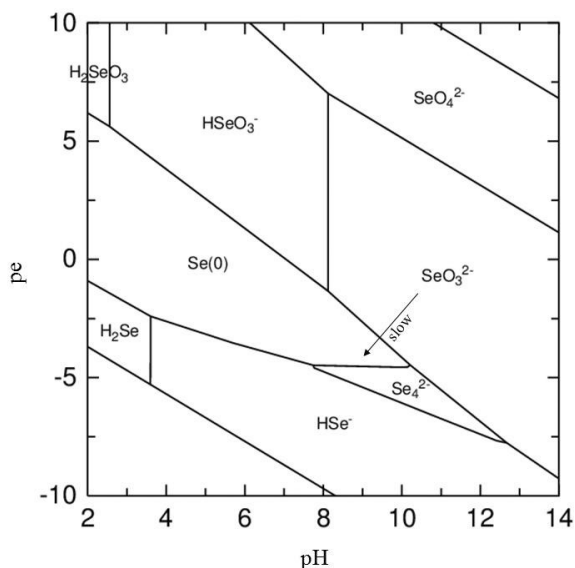
Fig. 1. Eh-pH diagram for 1.3×10^{-5} M selenium under the experimental conditions calculated by PHREEQC 3.0 code using the thermodynamic data from Iida et al. [25]. The arrow shows that the reduction of $Se(IV)O_3^{2-}$ into $Se(0)$ is a slow process.

Fig. 2. Ionic bonds of anions (Cl^-, CO_3^{2-}, and SO_4^{2-}) on the positive sites of $Fe(III)$ in the interlayer of GR.

where
$x = [Fe(III)] / ([Fe(II)] + [Fe(III)])$,
A^{n-} = donated interlayer anions with n^- charge, and
m = the mole of water molecules.

GR is a member of a family of minerals called Layered Double Hydroxides (LDH) and has been of interest owing to its potential application as an anion exchanger. LDH structured materials are usually used as anion exchangers with high selectivity by their inherent composition [19]. In the LDH structure of GR, Fe(III) produces a positive charge in the GR layers where the positive charge is balanced by anions such as Cl^-, CO_3^{2-}, and SO_4^{2-} existing in the interlayer of GR. The interlayer distance of GR depends upon the anion species and structure [20-22]. Different interlayer distances of GR according to the different anions in the interlayer of GR are shown in Fig. 2.

The sorption of anions onto GR can occur by anion exchange with interlayer anions of GR and chemical adsorption onto edge sites of GR, leading to the formation of surface complexes, depending on the types of GR, sorbing anions, and chemical conditions [23, 24]. In this study, we focused on the anion exchange process of GR rather than chemical adsorption. GR as an anion exchanger and a strong reducer can influence the migration of anions in geochemical conditions relevant to a radioactive waste repository. However, the sorption behaviors of GR are not fully understood. Therefore, the purpose of this paper is to investigate the sorption behavior of major anions such as selenite ($Se(IV)O_3^{2-}$), selenate ($Se(VI)O_4^{2-}$), and iodide (I^-) onto GR with different structural anions.

2. EXPERIMENTAL
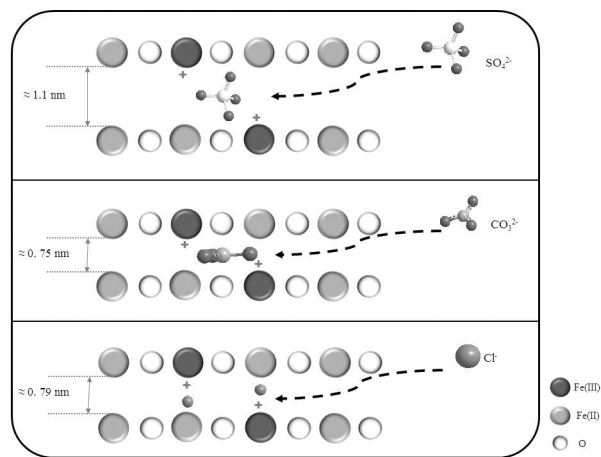
2.1 Materials and apparatus

All chemical solutions were prepared in nitrogen-purged deionized water with resistivity of 18.2 MΩ-cm (Milli-Q water (Millipore)). When GR was synthesized, airtight glass bottles with rubber stoppers were used to prevent the oxidation of Fe(II), because Fe(II) can easily oxidize into Fe(III) even in an anaerobic glove box. Polypropylene (PP) bottles were used for other stock solutions. All chemicals ($Na_2Se(IV)O_3$, $Na_2Se(IV)O_4$, NaI, $Fe(II)Cl_2 \cdot 4H_2O$, $Fe(III)Cl_3 \cdot 6H_2O$, Na_2CO_3, NaCl, and $NaClO_4$) used in the experiments were above pro-analysis grade.

All experiments were conducted in an anoxic glove box under a nitrogen and hydrogen atmosphere (96% N_2 and 4% H_2, O_2 < 10 ppm) at room temperature. A pH electrode (Orion 8103 B12) and an Eh electrode (Orion 9778 BMWP) connected with an electrometer (Orion 4 star) were used for pH and Eh measurements. The electrodes were calibrated using three pH buffer solutions (pH 4.01, 7.00, and 10.01) and one redox standard solution (+420 mV), respectively. After the sorption experiment, the solution was separated from the solid using polyethersulfone (PES) syringe micro-filters (Millipore) with a pore size of 0.22 μm. The concentrations of selenium and iodide were analyzed by inductively-coupled plasma optical emission spectrometry (ICP-OES, Thermo Scientific iCAP 6500 DUO) or inductively- coupled plasma mass spectrometry (ICP-MS, BRUKER 820-MS).

2.2 Synthesis of GR

2.2.1 GR carbonate, GR(CO₃²⁻)

GR carbonate, GR(CO₃²⁻), was synthesized using the method of Taylor et al. [25]. Two separate 100 mL solutions of 1 M Fe(II)Cl₂ · 4H₂O and 0.2 M Fe(III)Cl₃ · 6H₂O were maintained at pH 7 by adding an appropriate amount of 1 M Na₂CO₃ solution. The Fe(III)Cl₃ · 6H₂O solution was then added into the Fe(II)Cl₂ · 4H₂O solution and the mixed solution was thereafter maintained at pH 8 by adding 1 M Na₂CO₃ solution. The mixed solution of Fe(II)/Fe(III) was stirred for about 1 hour until a blue-green precipitate was formed. The blue-green precipitate (i.e., GR(CO₃²⁻)) was filtered in a vacuum under an anoxic condition and washed 3 to 4 times with Milli-Q water. The synthesized GR(CO₃²⁻) was immediately used in sorption experiments because it could change into magnetite or other iron oxides even in a glove box condition (O₂ < 10 ppm).

2.2.2 GR chloride, GR(Cl⁻)

GR chloride, GR(Cl⁻), was synthesized using the method of Refait et al. [26]. Fe(II)Cl₂ · 4H₂O in powder form (7.95 g) was dissolved in 70 mL of a 0.5 M NaCl solution. The prepared solution was adjusted to pH 7.5 using a 5 M NaOH solution. The solution was stirred for about 2 hours until the pH of the solution decreased to 6.5. A suspension solution containing precipitated Fe(II)(OH)₂(s) was thereby formed from the reaction of Fe(II)Cl₂ · 4H₂O with the NaOH solution while stirring the solution. A 1.0 M perhydroxide (H₂O₂) solution was injected slowly in the suspension solution of Fe(II)(OH)₂(s) according to a molar ratio of [Fe(II)Cl₂ · 4H₂O]/[H₂O₂] = 8.5 until a blue-green precipitate was formed. The blue-green precipitate (i.e., GR(Cl⁻)) was filtered in a vacuum under an anoxic condition and washed 3 to 4 times with Milli-Q water. Afterward, the GR(Cl⁻) particles were suspended again in Milli-Q water for sorption experiments. However, Cl⁻ still existed in the GR(Cl⁻) suspension with a concentration of about 50 mM after the aforementioned washing step with Milli-Q water. The synthesized GR(Cl⁻) suspension was immediately used in sorption experiments to avoid oxidation of the synthesized GR(Cl⁻).

2.3. Sorption experiments

2.3.1 Sorption of selenite and selenate

Two separate 20 mL solutions of 0.01 mM Na₂Se(IV)O₃ and 0.01 mM Na₂Se(VI)O₄ were prepared in a 10 mM NaClO₄ solution. GR(CO₃²⁻) in powder form (0.65 g) was added to the prepared solutions for the sorption reaction. In addition, 1 mM Na₂SiO₃ was introduced to investigate the effect of silicate ions on the sorption of selenium onto GR(CO₃²⁻). The pH of the solutions reacted with GR(CO₃²⁻) was adjusted to about 9 using 0.01 M and 0.1 M NaOH solutions during shaking for 1 hour. After the reaction time of 1 hour, the amount of selenium sorbed on the GR was calculated from the concentration difference between the initial and final concentrations of selenium in the solution. The reaction time of 1 hour was arbitrarily chosen for ease of experiments. The reaction time may be sufficient for the sorption reaction (particularly for anion exchange reaction) but insufficient for reduction of Se(IV) into Se(0).

In the presence of GR(CO₃²⁻), final Eh values of the reaction solutions ranged from -240 to -220 mV without the addition of a chemical reducer. A strong reducer (100 mM N₄H₂ and 20 mM Fe(II)Cl₂ · 4H₂O) was added to 1 mM Na₂Se(IV)O₃ solutions in the absence of GR(CO₃²⁻) to investigate the oversaturation solubility of Se(IV)O₃²⁻ owing to the reduction of Se(IV)O₃²⁻ into metal selenium, Se(0), under given experimental conditions (see Fig. 1).

2.3.2 Sorption of iodide

Some 20 mL solutions of 0.01 to 1 mM NaI were prepared in a 10 mM NaClO₄ solution. GR(CO₃²⁻) in powder form (0.65 g) was added to all prepared solutions for the sorption reaction. The pH of the reacting solutions containing GR(CO₃²⁻) was adjusted to about 9.0 using 0.01 M and 0.1 M NaOH solutions. Sorption experiments of iodide onto GR(CO₃²⁻) were conducted for 1.5, 72, and 168 hours. Final Eh values of the reaction solutions were measured as -240 to -220 mV in the presence of GR(CO₃²⁻) without the addition of a chemical reducer. The amount of iodide sorbed on the GR(CO₃²⁻) was calculated from the concentration difference between the initial and final concentrations of iodide in the solution.

A sorption experiment was also carried out to investigate the effect of dissolved Cl⁻ on the I⁻ sorption onto GR(Cl⁻) as a function of the [Cl⁻]/[I⁻] ratio. For the experiment, 12.5 mL solutions of 0.260 to 10 μM NaI were added to a 5 mL solution of GR(Cl⁻) and 7.5 mL solutions of 86 to 260 μM NaI were added to a 10 mL solution of GR(Cl⁻). The concentration of Cl⁻ in the solution was controlled by adjusting the volume of GR(Cl⁻)

added, because the GR(Cl⁻) suspension was stored in a 50 mM NaCl solution. The amount of GR(Cl⁻) existing in the suspension solution was determined to be 0.25 g after freeze-drying the 10 mL suspension solution.

The pH of the reaction solutions was adjusted to 7.5 to 8 using 0.1 M and 1.0 M NaOH solutions. Sorption experiments of iodide onto GR(Cl⁻) were conducted for 1, 14, and 96 hours. The final Eh values of the reaction solutions were measured as about -400 mV in the presence of GR(Cl⁻) without the addition of a chemical reducer.

3. RESULTS AND DISCUSSIONS

3.1 Sorption of selenite onto GR(CO₃²⁻)

Experimental conditions and results for the sorption of $Se(IV)O_3^{2-}$ onto GR(CO₃²⁻) are shown in Table 1. It is well known that $Se(IV)O_3^{2-}$ can be reduced to Se(0) in a strong reduction condition [4, 14, 27-30]. Oversaturation solubility experiments of $Se(IV)O_3^{2-}$ were thus carried out to determine the initial concentration of $Se(IV)O_3^{2-}$ before the sorption experiments. As shown in Table. 1, the oversaturation solubility of $Se(IV)O_3^{2-}$ was measured as 0.42 mM in a 100 mM N₂H₄ solution (pH 9.81 and Eh = -310 mV for 7 days) and as 0.61 mM in a 20 mM Fe(II)Cl₂ · 4H₂O solution (pH 4.7 and Eh = -170 mV for 1 hour) when the initial concentrations of $Se(IV)O_3^{2-}$ were 1 mM and 0.95 mM for the two solutions, respectively. Thus we used a much lower initial concentration of $Se(IV)O_3^{2-}$, 1.3×10^{-5} M, than the measured oversaturation solubility values for the sorption experiments to avoid precipitation of $Se(IV)O_3^{2-}$ as Se(0) by reduction.

The solubility of selenite greatly depends upon the redox condition above pH 8, especially in the vicinity of the boundary conditions of Se(0) [27] (see Fig. 1). In fact, the initial concentration of $Se(IV)O_3^{2-}$ (i.e., 1.3×10^{-5} M) was expected to be higher than the solubility of Se(0) at pH 9 and Eh = -240 to -220 mV. However, some studies reported that reduction of $Se(IV)O_3^{2-}$ to Se(0) is a slow process even in the presence of reducing agents such as Fe(II)-containing minerals and reducing bacteria [28, 29]. For instance, Myneni et al. [30] reported that $Se(VI)O_4^{2-}$ was rapidly reduced to $Se(IV)O_3^{2-}$ by GR(SO₄²⁻) but the formed $Se(IV)O_3^{2-}$ was slowly reduced to Se(0) by GR(SO₄²⁻). Recently, Schellenger and Larese-Casanova [24] reported that Se(VI) was reduced rapidly but Se(0) formed very slowly. It was also reported from an experiment using GR(SO₄²⁻) that sorption is a major removal mechanism for Se(IV) and reduction is not necessarily the dominant removal process [31]. In our experimental system, all sorption experiments were conducted for 1 hour. The possibility $Se(IV)O_3^{2-}$ being reduced to Se(0) thus appears to be very low because the reduction of Se(IV) to Se(0) would be a slow process that may require more than 1 hour. Table 1 shows that most of the $Se(IV)O_3^{2-}$ was removed quickly from the solution during 1 hour by GR(CO₃²⁻). It can thus be presumed that the removal of $Se(IV)O_3^{2-}$ from the solution is due to sorption onto GR(CO₃²⁻), not to reduction to Se(0).

As shown in Table 1, most of the $Se(IV)O_3^{2-}$ was removed from the solutions regardless of the pre ence of silicate ions, which dominantly exist as H₄SiO₄ at given conditions. It was reported that H₄SiO₄ dissolved in a solution can hinder the chemical adsorption of $Se(IV)O_3^{2-}$ onto iron oxide [3, 32]. However, in this study, the sorption of $Se(IV)O_3^{2-}$ onto GR(CO₃²⁻) was not

Table 1. Experimental conditions and results for the sorption of selenium onto synthesized GR(CO₃²⁻)

GR(CO₃²⁻) (g/L)	[Se]ᵢₙᵢₜᵢₐₗ(M)		Na₂SiO₃ (M)	pH_final	Eh_final (mV)	Reducing agent	[Se]_final (M)	[Se]_sorbed (%)
	$Se(IV)O_3^{2-}$	$Se(VI)O_4^{2-}$						
-	1.0×10^{-3}	-	-	9.81	-310	100 mM N₂H₄	4.2×10^{-4}	
-	9.5×10^{-4}	-	-	4.7	-170	20 mM Fe(II)Cl₂	6.1×10^{-4}	
32.5	1.3×10^{-5}	-	1.0×10^{-3}	9.00	-240 - -220	-	2.0×10^{-7}	98
	1.3×10^{-5}	-	1.0×10^{-3}	8.90			2.4×10^{-7}	98
	1.3×10^{-5}	-	-	8.91			3.4×10^{-7}	97
	1.3×10^{-5}	-	-	8.96			3.9×10^{-7}	97
32.5	-	1.4×10^{-5}	1.0×10^{-3}	8.98	-240 - -220	-	7.9×10^{-6}	44
	-	1.4×10^{-5}	1.0×10^{-3}	9.03			8.8×10^{-6}	37
	-	1.4×10^{-5}	-	9.00			7.9×10^{-6}	44
	-	1.4×10^{-5}	-	9.00			1.0×10^{-5}	29

※ All experiments were conducted in 10 mM NaClO₄ solution.

affected by the presence of H_4SiO_4 even at a 100 times higher concentration than that of $Se(IV)O_3^{2-}$. It is thus surmised that a sorption process other than chemical adsorption can occur during the sorption of $Se(IV)O_3^{2-}$ onto $GR(CO_3^{2-})$. When $Se(IV)O_3^{2-}$ is reacted with $GR(CO_3^{2-})$, the anion $Se(IV)O_3^{2-}$ can be exchanged with CO_3^{2-} existing in the interlayer of $GR(CO_3^{2-})$ by an anion exchange process. This anion exchange mechanism of $Se(IV)O_3^{2-}$ with $GR(CO_3^{2-})$ can be explained by $Se(IV)O_3^{2-}$ having the same geometry (a planar structure) and charge as CO_3^{2-} existing in the interlayer of $GR(CO_3^{2-})$. Thus, as shown in Table 1, $Se(IV)O_3^{2-}$ was considered to be mostly sorbed on $GR(CO_3^{2-})$ by an anion exchange process.

3.2 Sorption of Selenate onto GR(CO₃²⁻)

Experimental conditions and results for the sorption of $Se(VI)O_4^{2-}$ onto $GR(CO_3^{2-})$ are also shown in Table 1. In the case $Se(VI)O_4^{2-}$, much lower sorption onto $GR(CO_3^{2-})$ than that of $Se(IV)O_3^{2-}$ was expected since $Se(VI)O_4^{2-}$ has a different geometry (a three dimensional structure) from CO_3^{2-} and a larger volume [33]. However, as shown in Table 1, about 30 to 45% of $Se(VI)O_4^{2-}$ was sorbed onto $GR(CO_3^{2-})$ within 1 hour regardless of the presence of SiO_3^{2-}, contrary to our prediction of low sorption of $Se(VI)O_4^{2-}$ onto $GR(CO_3^{2-})$ due to the differences in physical properties between $Se(VI)O_4^{2-}$ and CO_3^{2-} existing in the interlayer of $GR(CO_3^{2-})$. As previously mentioned, $Se(VI)O_4^{2-}$ can be reduced to $Se(IV)O_3^{2-}$ and/or $Se(0)$ by the Fe(II) present in $GR(CO_3^{2-})$ depending on reaction kinetics. The notable sorption of $Se(VI)O_4^{2-}$ onto $GR(CO_3^{2-})$ can thus be explained by the following two sequential processes: (1) $Se(VI)O_4^{2-}$ may be reduced to $Se(IV)O_3^{2-}$ by Fe(II) existing on the external surface sites

of $GR(CO_3^{2-})$, and (2) the reduced $Se(IV)O_3^{2-}$ from $Se(VI)O_4^{2-}$ will be sorbed onto $GR(CO_3^{2-})$, because $Se(IV)O_3^{2-}$ can be quickly exchanged with CO_3^{2-} existing in the interlayer of $GR(CO_3^{2-})$. Otherwise, $Se(VI)O_4^{2-}$ can be removed from the solution by direct reduction to $Se(0)$, but this may not be a favorable mechanism for the removal of $Se(VI)O_4^{2-}$ during the considered reaction time of 1 hour [30, 31].

3.3 Sorption of iodide onto GR(CO₃²⁻)

The sorption of I^- onto $GR(CO_3^{2-})$ was conducted in 10 mM $NaClO_4$ with varying concentrations from 0.01 to 1 mM for 1.5, 72, and 168 hours. I^- is expected to exist mostly as dissolved species because its solubility is very high at both oxidized and reduced conditions [34]. It is known that I^- can be sorbed onto strong cation sites ($\equiv FeOH_2^+$) of iron oxides of pH usually below 5, forming outer-sphere surface complexes [15]. However, I^- will not be sorbed on weak cation sites ($\equiv FeOH$) and anion sites ($\equiv FeO^-$) of iron oxides of pH usually above 5 [15]. Anion exchange between I^- and CO_3^{2-} existing in the interlayer of $GR(CO_3^{2-})$ was expected to occur, such as $Se(IV)O_3^{2-}$. However, as shown in Fig. 3, the removal of I^- was not observed. Based upon the assumption that the sorption of I^- onto $GR(CO_3^{2-})$ occur by an anion exchange process, this different sorption behavior of I^- from $Se(IV)O_3^{2-}$ can be explained by the differences in their physical and chemical properties. CO_3^{2-} has a planar geometry and -2 charges whereas I^- has a monomolecular structure and -1 charge. The different physical and chemical properties of I^- from CO_3^{2-} would thus impede diffusion of I^- into the interlayer of $GR(CO_3^{2-})$, and exchange with CO_3^{2-} existing in the interlayer of $GR(CO_3^{2-})$ thus does not readily occur.
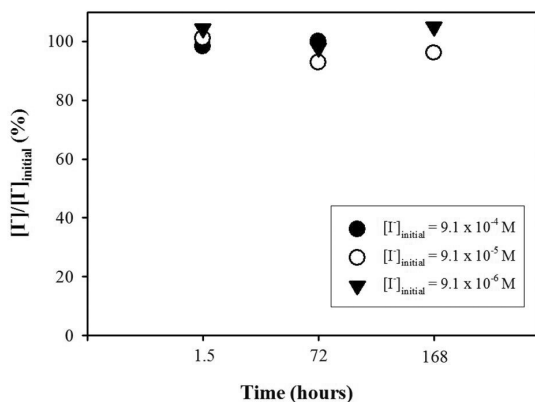

Fig. 3. The percentage of I^- remaining in the solution in presence presence of $GR(CO_3^{2-})$ as a function of contact time at $NaClO_4$ = 10 mM and $m_{GR(CO_3^{2-})}/V_{sol}$ = 33 - 37 g/L.
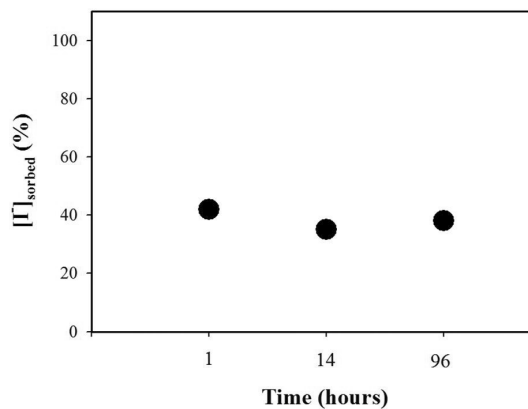

Fig. 4. The percentage of I^- sorbed onto $GR(Cl^-)$ as a function of contact time at $NaClO_4$ = 10 mM and $m_{GR(CO_3^{2-})}/V_{sol}$ = 12.5 g/L.

Table 2. Experimental conditions and results for the sorption of iodide onto synthesized GR(Cl$^-$)

GR(Cl$^-$) (g/L)	[I$^-$]$_{initial}$ (M)	[Cl$^-$]$_{initial}$ (M)	[Cl$^-$]/[I$^-$]	pH$_{final}$	Eh$_{final}$ (mV)	[I$^-$]$_{final}$ (M)	[I$^-$]$_{initial}$-[I$^-$]$_{final}$ (M)	[I$^-$]$_{sorbed}$ (%)
14.3	2.6×10^{-4} 8.6×10^{-5}	2.8×10^{-2}	1.1×10^2 3.3×10^2	7.67 7.57	-400	2.1×10^{-4} 4.9×10^{-5}	5.2×10^{-5} 3.7×10^{-5}	20 43
7.2	1.0×10^{-5} 1.0×10^{-6} 2.6×10^{-7}	1.4×10^{-2}	1.4×10^3 1.4×10^4 5.5×10^4	7.90 7.89 7.90	-400	7.1×10^{-6} 7.7×10^{-7} 2.0×10^{-7}	3.3×10^{-6} 2.6×10^{-7} 6.3×10^{-8}	28 23 22

※ All experiments were conducted in 10 mM NaClO$_4$ solution.

3.4 Sorption of iodide onto GR(Cl$^-$)

As shown in Fig. 4, the sorption of I$^-$ onto GR(Cl$^-$) occurred quickly, within 1 hour, although the sorption experiment was conducted for 1, 14, and 96 hours. Experimental conditions and results for the sorption of I$^-$ onto GR(Cl$^-$) are shown in Table 2. As shown in Table 2, about 20 to 43% of I$^-$ was sorbed onto GR(Cl$^-$); this result is very different from that of GR(CO$_3^{2-}$), which showed no sorption of I$^-$. This difference in the sorption behavior of I$^-$ for GR(Cl$^-$) and GR(CO$_3^{2-}$) may be due to I$^-$ having the same geometry and charge as Cl$^-$. The amount of I$^-$ sorbed onto GR(Cl$^-$) as a function of the [Cl$^-$]/[I$^-$] ratio is shown in Fig. 5. The results show a linear relationship between [I$^-$]$_{sorbed}$ and [Cl$^-$]/[I$^-$]. This linear relationship implies that the sorption of I$^-$ onto GR(Cl$^-$) depends on the concentration of Cl$^-$ dissolved in solution, which competes with I$^-$ against sorption onto GR(Cl$^-$). Consequently, I$^-$ and Cl$^-$ dissolved in solution will be competitively exchanged with Cl$^-$ existing in the interlayer of GR(Cl$^-$). In addition, GR(Cl$^-$) exchanged with I$^-$ will be changed into GR(I$^-$). This dependency of I$^-$ sorption on the concentration of Cl$^-$ dissolved in solution also supports the finding that the sorption of I$^-$ onto GR(Cl$^-$) mainly occurred by an anion exchange process between I$^-$ and Cl$^-$.

4. CONCLUSION

The sorption of iodide and selenium onto green rust was studied to investigate the influence of green rust on the migration of anions such as selenite, selenate, and iodide considering different structures of green rust, i.e., GR(Cl$^-$) and GR(CO$_3^{2-}$). The experimental results showed that most Se(IV)O$_3^2$ was sorbed onto GR(CO$_3^2$) within 1 hour by anion exchange with CO$_3^2$ existing in the interlayer of GR(CO$_3^2$), regardless of the presence of SiO$_3^{2-}$. Some of the Se(VI)O$_4^{2-}$ was removed from the solution within 1 hour and this removal was presumed to be due to the sorption of Se(IV)O$_3^2$ onto GR(CO$_3^2$) following the reduction of Se(VI)O$_4^{2-}$ into Se(IV)O$_3^2$ by structural Fe(II) of GR(CO$_3^2$). For the sorption of I$^-$ onto GR(Cl$^-$), I$^-$ was quickly sorbed onto GR(Cl$^-$) within 1 hour by anion exchange with Cl$^-$ existing in the interlayer of GR(Cl$^-$). However, I$^-$ was not sorbed onto GR(CO$_3^2$) due to the different physical and chemical properties of I$^-$ from CO$_3^2$ existing in the interlayer of GR(CO$_3^2$).

In geological environments, GR(CO$_3^2$) can be formed in groundwater with a high carbonate concentration and GR(Cl$^-$) can be formed in groundwater near seawater or saline layers. The sorption of selenite and iodide onto GR(CO$_3^2$) and GR(Cl$^-$), respectively, mainly occurs by anion exchange between the anionic radionuclides and the anions existing in the interlayer of GR(CO$_3^2$) and GR(Cl$^-$). Green rusts may therefore play an important role in the retardation of anionic radionuclides such as selenite, selenate, and iodide depending upon the structural anions in radioactive waste disposal environments owing to their strong reducing potential by structural Fe(II) and anionic exchange capacity by the LDH structure.
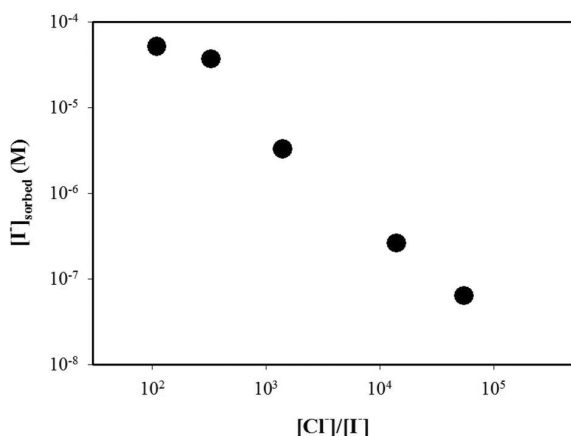

Fig. 5. The amount of I$^-$ sorbed onto GR(Cl$^-$) as a function of [Cl$^-$]/[I$^-$] ratio dissolved in solution at NaClO$_4$ = 10 mM and m$_{GR(CO_3^2)}$/V$_{sol}$ = 7.1 - 14.2 g/L .

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