

## Interruption with the Migration of Iodide by GR(Cl)

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### 1. Introduction

In underground radioactive waste repository, the corrosion of iron canisters would be proceed as follows; Fe(II) and/or Fe(III) dissolved from iron containers  $\rightarrow$  Fe(II)(OH)<sub>2</sub> and/or Fe(III)(OH)<sub>3</sub>  $\rightarrow$  Green rust  $\rightarrow$  Lepidocrocite or Magnetite  $\rightarrow$  Goetite etc. Generally, the green rust has known to exist in environments close to the Fe(II)/Fe(III) transition zone or between the oxidized layer and reduced layer in the underground. As anion exchanger and strong reducer, the green rusts can affect the migration of anions in underground radioactive waste repository. Despite green rusts are important on the migration of anions, reactions involving green rusts were poorly studied in relation to the safety assessment of radioactive waste repository. The purpose of this study is to understand the influence of green rust on the migration of iodide(I).

### 2. Experiment

#### 2.1 Synthesis of GR(Cl)

Green rust chloride(GR(Cl)) was synthesized using the method from Ph. Refait et al[1]. 40 mmole of FeCl<sub>2</sub> · 4H<sub>2</sub>O powder was dissolved in 0.5 mole/L NaCl 70 mL solution. The acidity of prepared solution was adjusted at pH 7.5 by addition of 5 mole/L NaOH. The solution was magnetically stirred for approximately 2 hours to obtain precipitated Fe(OH)<sub>2</sub>(s) suspension and its pH was measured about 6.5. Perohydroxide (1 mole/L) solution was injected in precipitated Fe(OH)<sub>2</sub>(s) solution as FeCl<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> = 8.5 mole ratio. The precipitated blue-green rust was vacuum filtered under anoxic condition and washed with deionized water 3 ~ 4 times. The filtered suspension of solution including GR(Cl) is used to sorption experiments, immediately.

#### 2.2 Reaction of between iodide and GR(Cl)

Separate solutions of  $2.6 \times 10^{-7}$  to  $2.6 \times 10^{-4}$  mmole/L NaI were prepared in the glass bottles with rubber stopper. The GR(Cl) suspension (5 or 10 mL) was added to the NaI solution, in which the dry weight of 10 mL GR(Cl) suspension was 0.25 g. The sorption experiments were conducted for 1, 14, and 336 hours, respectively. The redox potential of solutions was measured about -400 mV without addition of reducing agent.

### 3. Results

As shown in Fig. 1, the most sorption between iodide and GR(Cl) are quickly occurred within 1 hour.

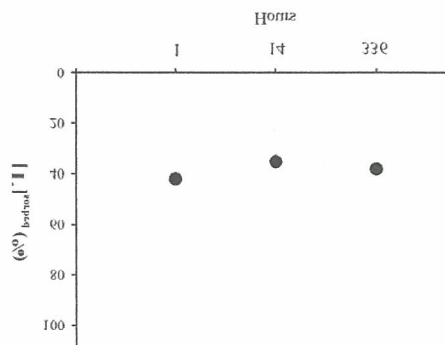


Fig. 1. Fraction of iodide as a function of reaction time at  $[I^-]_{\text{initial}} = 8.6 \times 10^{-5}$  mole/L and GR(Cl)/solution = 12.5 g/L.

Sorbed rate of iodide on GR(Cl) as function of concentration are showed in Table 1. Despite GR(Cl) was washed with deionized water 3 ~ 4 times, some of chloride could be still dissolved in the suspension of GR(Cl). Hence, the chloride as a form of dissolve in the solution or sorbed by GR(Cl) could compete with iodide for the sorption

Table 1. The experimental conditions and results for the sorption of iodide on GR(Cl) as a function of iodide concentration.

Suspension solution (mL)	[I] <sub>Initial</sub> (mole/L)	[Cl] <sub>Initial</sub> (mole/L)	[Cl]/[I]	Final pH	Final Eh (mV)	[I] <sub>Final</sub> (mole/L)	$\frac{[I]_{\text{initial}} - [I]_{\text{final}}}{[I]_{\text{initial}}}$ (mole/L)	[I] <sub>sorbed</sub> (%)
10	-	4.9x10 <sup>-3</sup>	-	7.59	-400	x	x	x
	2.6x10 <sup>-4</sup>	2.8x10 <sup>-3</sup>	1.1x10 <sup>2</sup>	7.67		2.1x10 <sup>-4</sup>	5.2x10 <sup>-5</sup>	20
	8.6x10 <sup>-5</sup>		3.3x10 <sup>2</sup>	7.57		4.9x10 <sup>-5</sup>	3.7x10 <sup>-5</sup>	43
5	1.0x10 <sup>-5</sup>	1.4x10 <sup>-3</sup>	1.4x10 <sup>3</sup>	7.90		7.1x10 <sup>-6</sup>	3.3x10 <sup>-6</sup>	28
	1.0x10 <sup>-6</sup>		1.4x10 <sup>4</sup>	7.89		7.7x10 <sup>-7</sup>	2.6x10 <sup>-7</sup>	23
	2.6x10 <sup>-7</sup>		5.5x10 <sup>4</sup>	7.90		2.0x10 <sup>-7</sup>	6.3x10 <sup>-8</sup>	22

\* (-) : No added in experience solution, (x) : No measured

of iodide onto anionic sorption site of GR(Cl). The most sorbed rate of iodide are slightly reduced according to increased rate of [Cl]/[I] only except on [I]<sub>initial</sub>=2.6x10<sup>-4</sup> mole/L. The most sorbed iodide concentration on GR(Cl) is about 5.2 x 10<sup>-5</sup> mole/L in Table 1.

#### 4. Discussion

The mechanism of the reduced iodide by GR(Cl) is assumed precipitation and/or adsorption on the surface reactive sites of GR(Cl) and/or anion exchange between anion(Cl) in interlayer of GR(Cl) and iodide.

Solid precipitation of iodide as I(cr) or FeI<sub>2</sub>(cr) is never occurred because I(cr) and FeI<sub>2</sub>(cr) have high solubility at oxidation and reduction conditions. In general, iodide is known that can be adsorbed as outer-sphere on the strong cation site(≡FeOH<sub>2</sub><sup>+</sup>) of iron oxide below pH 5. However, iodide is rarely sorbed on the weak cation site(≡FeOH) and anion site(≡FeO<sup>-</sup>) of the iron oxide above pH 5[2]. At pH 9, formed major surface sites(≡FeOH and/or ≡FeO<sup>-</sup>) of iron oxide can't remove the iodide. However, the concentration of iodide was dramatically decreased by addition of GR(Cl). It suggested that the dissolved iodide in solutions were exchanged with the chloride in interlayer of GR(Cl).

It's that although 1.4x10<sup>-3</sup> to 2.8x10<sup>-3</sup> mole/L chloride is dissolved with 2.9x10<sup>-7</sup> to 2.6x10<sup>-4</sup> mole/L iodide in the separate solutions, the iodide is

exchanged with chloride in interlayer of GR(Cl) and sorbed on the positive site of GR(Cl). Although the characteristics of GR(Cl) were not analyzed in this work because GR(Cl) is very sensitive against oxidation, iodide migration may be interrupted near the seawater or saline layer by the GR(Cl) as a iron corrosion product.

#### 5. Conclusions

GR(Cl) would be major corrosion product of iron near the seawater or saline layer in underground. The GR(Cl) may play an important role in the retardation of the iodide migration in a deep geological environment due to it's anionic exchange reaction.

#### 6. Reference

- [1] Ph. Refait, O. Benali, M. Abdelmoula, J.-M.R. Genin, Formation of 'ferric green rust' and/or ferrihydrite by fast oxidation of iron(II-III) hydroxychloride green rust, Corrosion science 45 (2003) 2435-2449.
- [2] T. Nagata, K. Fukushi, Y. Takahashi, "Prediction of iodide adsorption oxides by surface complexation modeling with spectroscopic confirmation" J. Colloid and inter. Sci. 332, (2009) 309-316.