The Sorption of Selenate and Selenite onto Magnetite in the Carbonate Solution

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1. Introduction

The long-lived (half-life: 6.5×10^4 years) radionuclide ^{79}Se has been concerned as one of the interest nuclides in a disposal system of the radioactive waste. Naturally selenium exists as four different oxidation states with different chemical behaviors: selenide(Se^{II}), elemental selenium(Se^0), selenite($Se^{IV}O_3^{2-}$) and selenate($Se^{VI}O_4^{-2}$). While metal selenide and elemental selenium have a very low solubility, selenite and selenate are soluble and mobile [1].

The metal canister containing high-level wastes or spent fuels would be disposed in a borehole or tunnel located a deep underground according to a Korean concept. In this geological condition, the iron canister will be corroded into magnetite [2]. Since studies on selenium sorption have indicated that it can be strongly adsorbed by iron oxyhydroxides and oxides, retention of selenite and selenate on the magnetite could then be possible due to immobilization process [3]. However several anions in groundwater, especially carbonate with high concentration in KAERI Underground Research Tunnel (KURT) groundwater [4], can compete with selenium oxides for the sorption onto iron corrosion products.

In this work, the sorption of selenate and selenite onto magnetite was studied in various pH solutions with and without carbonate ion. Then the results were applied for surface complexation modeling.

2. Experiment and Modeling

All experiments have been performed at room temperature in an Ar-filled glove. Selenite and selenate solutions of 1.0×10^{-5} mol/L were prepared by dissolving Na_2SeO_3 and Na_2SeO_4, respectively, in 0.02 M $NaClO_4$ matrix. To understand the carbonate effect on selenium sorption, some solutions were adjusted to be 1.0×10^{-3} mol/L of Na_2CO_3. The carbonate concentration is the similar to KURT groundwater. 1.0 g of magnetite was put in 20 mL of a prepared solution in polypropylene bottle. Then the pH of solutions was adjusted to 7 ~ 11 with a dilute $HClO_4$ or NaOH solution. The solution was shaken for 3 to 7days.

After shaking for the time, the solution was filtered with a 0.2 μm polyethersulfone (PES) filter. Selenium concentration in solution was determined by inductively coupled plasma-mass spectrometry (ICP-MS).

Specific surface area of magnetite was determined by applying the BET equation, and the results are Table 1. FITEQL 4.0 code was used for the modeling of selenite sorption on the magnetite from experimentally obtained results.

Table 1. Surface Characteristics of Magnetite

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BET surface area	5.11 m^2/g
Reactive site concentration	1.06×10^{-3} mol/L
Solid concentration	50 g/L

3. Results and Discussion

Almost selenate was not sorbed onto magnetite in the pH 7 ~ 11. The percentage of selenite sorbed onto magnetite, $[Se]_{sorb}$(%), was calculated according to the following equation, and the results as a function of pH are shown in Fig. 1.

$$[Se]_{sorb}(\%) = \frac{[Se]_{ini} - [Se]_{re}}{[Se]_{ini}} \times 100 \quad \text{............(1)}$$

$[Se]_{ini}$: initial selenium concentration
$[Se]_{re}$: selenium concentration in a filtrate after equilibrium

When the species {=FeOSe(O)OH} was considered as a main selenite adsorption structure onto magnetite [5], we obtained the best fit by modeling with only one mechanism as following;

$$\text{............(2)}$$
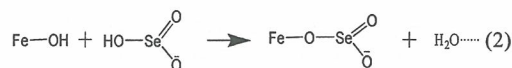
The thermodynamic equilibrium constants in Table 2 were used for the modeling. From the diffusion double layer model (DDLM) by using FITEQL 4.0 code [6], the equilibrium constants ($Log\ K$) for the surface complexes between selenite and magnetite were obtained as 7.73 and 7.25 in the solutions with and without carbonate, respectively.

Distribution of selenium species in 1.0 M $NaClO_4$ with total selenium at 1.0 M Na_2SeO_3 are known 56% $HSeO_3^-$ and 44% $H_2(SeO_3)_2^{2-}$ at pH 5.0, and 32% SeO_3^{2-}, 28% $H_2(SeO_3)_2^{3-}$, 24% $H_2(SeO_2)_2^{2-}$ and 16% $HSeO_3^-$ at pH 8.0. However, selenate was not adsorption onto magnetite because free SeO_4^{2-} anion is the only predominant species at pH 5.0 and 8.0. [7]
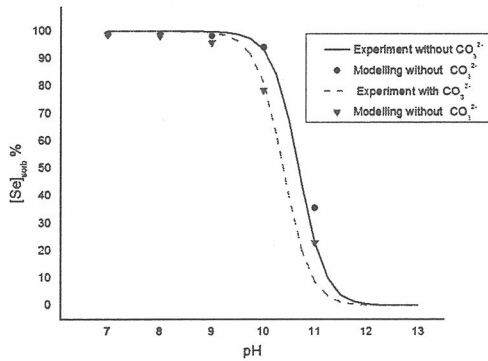
Fig. 1. Sorption of selenite onto magnetite as a function of pH. $[Se]_{ini} = 1x10^{-5}$ mol/L, magnetite=50 g/L, $2x10^{-2}$ mol/L $NaClO_4$ matrix, reactive site concentration of magnetite = $1.06x10^{-3}$ mol/L.

Table 2. Thermodynamic Equilibrium Constant for Several Reactions.

Reaction	Log K
$SeO_3^{2-} + H^+ \leftrightarrow HSeO_3^-$	8.36 (OECD/NEA)
$HSeO_3^- + H^+ \leftrightarrow H_2SeO_3$	2.6 (OECD/NEA)
$FeOH + H^+ \leftrightarrow FeOH_2^+$	5.1 (NEM)
$FeO^- + H^+ \leftrightarrow FeOH$	9.1 (NEM)
$CO_3^{2-} + H^+ \leftrightarrow HCO_3^-$	10.33 [8]
$HCO_3^- + H^+ \leftrightarrow H_2CO_3$	6.35 [8]

4. Conclusions

The sorption reaction of both selenate and selenite onto magnetite at room temperature was reached to equilibrium within 3 days.

Sorption of selenite onto magnetite was decreased with increasing pH since the ratio of hydrated selenite species might be reduced. However little sorption of selenate was found at pH 7 ~ 11 because of the existence of free SeO_4^{2-} as only predominant species in the pH range. Carbonate ion in the solution affected the selenite adsorption onto magnetite.

5. References

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