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Effects of pH and anions on the sorption of selenium ions onto magnetite

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ABSTRACT

This study analyzes the influence of carbonate and silicate, which are generally abundant in granitic groundwater, on the sorption of selenium ions onto magnetite in order to understand the behaviors of selenium in a radioactive waste repository. Selenite was sorbed onto magnetite very well below pH 10, but silicate and carbonate hindered the sorption of selenite onto magnetite. On the other hand, little selenate was sorbed onto magnetite in neutral and weak alkaline solutions of 0.02 M $NaNO_3$ or $NaClO_4$, matching the ionic strength in a granitic groundwater, even though silicate or carbonate was not contained in the solutions. The surface complexation constants between selenite and magnetite were obtained by using a geochemical program, FITEQL 4.0, from the experimental data, and the formation of an inner-sphere surface complex such as $\equiv FeOSeO_2^-$ was suggested for the sorption of selenite onto magnetite from the diffuse double layer model calculation.

1. Introduction

Safety assessments of high-level radioactive waste disposal in deep underground repositories have frequently considered the nuclide ^{79}Se because of its long halflife ($t_{1/2} = 1.1 \times 10^6$ years) (Hwang and Kang, 2010; Ishikawa et al., 2008). Selenium exists naturally in four different oxidation states with very 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 selenides and elemental selenium have a very low solubility and are fairly immobile, selenite and selenate are soluble and mobile. Selenium is likely to exist under three oxidation states (−II, 0, IV) in a reducing environment, and Se(−II) is likely to precipitate in the presence of Fe(II) (Jordan et al., 2009).

Owing to their negative charge, selenite and selenate adsorb to Fe(III) oxides (Scheinost et al., 2008), but they are only weakly sorbed by clay minerals with prevalent cation exchange capacity (Duc et al., 2003; Martinez et al., 2006), iron oxides such as hematite (Duc et al., 2006; Rovira et al., 2007), goethite (Martinez et al., 2006; Su and Suarez, 2000), and magnetite (Martinez et al., 2006) are known to be capable of binding selenite with high distribution coefficients in groundwater. Moreover, the presence of Fe(II) in magnetite has been shown to help reduce selenium oxyanions to a lower oxidation state (Charlet et al., 2007; Scheinost et al., 2008). However, X-ray absorption spectroscopy indicated that the oxidation state of selenium did not change when selenite adsorbed onto magnetite at pH 4.45–7.46 (Missana et al., 2009). Thus, there are still many questions regarding the reduction of selenite by magnetite.

Based on the Korean disposal concept, a metal canister (depth = 483 cm, inner diameter = 100 cm and thickness = 10 cm) containing high-level radioactive wastes or spent fuels would be installed in a cylindrical clay block (wall thickness = 30–50 cm) that will be placed in the borehole or tunnel located deep underground (Choi et al., 2007). The proposed disposal canister would be made of iron, and its outside coated with a corrosion-resistant metal such as copper (Choi et al., 2010). Under deep geological conditions, the iron canister will corrode into magnetite (Missana et al., 2009). Then, magnetite may sorb the mobile selenium species such as selenate or selenite released from wastes or spent fuel. However, the sorption of selenate or selenite onto magnetite can be hindered by other anions in groundwater.

Fujikawa and Fukui (1997) showed that a high concentration of sulfate, as compared to selenium, reduced the sorption of selenite onto hematite and magnetite. On the contrary, Goh and Lim (2004) discovered that sulfate, when simultaneously introduced in the

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suspension, has an inconsequential influence on the adsorption of selenite on a Singapore soil that contained a significant amount of iron. The authors found that the presence of phosphate ions led to a competition effect between PO_4^{3-} and selenium oxyanions for surface sites of the soil, which was presumably due to both the formation of surface complexes and the surface accumulation or precipitation of the PO_4^{3-} species. Balistrieri and Chao (1990) also studied the competition effect of various anions such as phosphate, silicate, molybdate, and sulfate on the sorption of selenite onto goethite at pH 7.0, and they found that silicate ion acted as a strong competitor. However, the influence of carbonate is not understood though the concentration of carbonate (+bicarbonate) is higher than those of other anions in a domestic granitic groundwater (Kim et al., 2010).

This study analyzed how carbonate and silicate act as competitors to influence the sorption of selenite and selenate on magnetite in order to better understand the behavior of selenium in a radioactive waste repository. The variations of the selenite sorption according to pH in the solutions with and without carbonate also were modeled and analyzed using a surface complexation model.

2. Experimental

2.1. Materials

The specific surface area of magnetite (Fe_3O_4) powder (from Showa in Japan) was obtained by applying the Brunauer–Emmet–Teller (BET) equation with nitrogen adsorption isotherms measured by using a Micrometrics ASAP instrument. Deionized Milli-Q water (Millipore) was used in this study. Selenite and selenate stock solutions were prepared by dissolving Na_2SeO_3 and $Na_2SeO_4{\cdot}10H_2O$ (both from Aldrich) in water, respectively. For the sorption test at less than 5×10^{-4} mmol/L (mM) of selenite, a selenite solution with Se-75 isotope (from EcKert & Ziegler Isotope Products) having 2 Ci/g of specific activity was diluted. Two kinds of electrolyte media, $NaNO_3$ and $NaClO_4$, were prepared with $NaNO_3$ (from Showa) and $NaClO_4{\cdot}H_2O$ (from Merck), respectively. All other reagents used were above pro-analysis grade, and all stock solutions were kept in Teflon® bottles.

2.2. Sorption experiment

Solution preparation, sorption reaction, and sample filtration were performed in an Ar-filled glove box at a room temperature. In 30 mL polypropylene bottles, 1 g of magnetite was immersed in 20 mL of the prepared solutions which contained the electrolytes, the selenium ion, and the other anions. The pH of the solution was then adjusted by adding a small amount of either NaOH or $HClO_4$ solution. In a preliminary test to estimate the equilibrium time between the sorbent and the selenium ions, the concentration of the selenium in the solution remained unchanged after three days reaction time. Thus the bottles were shaken for the sorption reaction for seven days. Just after sampling, the final pH of the solutions was measured in the glove box.

After sorption reaction, the suspension was filtered through polyethersulfone (PES) micro-filters with 0.22 μm pore size. To remove the colloids, some of the micro-filtered solutions were then filtered again using an NMWL 10 k ultrafiltration membrane (PES, Millipore). In order to observe the sorption of selenium by the polypropylene bottle and the PES filter, a blank test was also performed without adding magnetite. The sample solutions were removed from the glove box, and 20 μL aliquots of concentrated

Table 1
The experimental conditions and results for the preliminary test of the sorption of selenium ions onto magnetite.

Magnetite (g)	Initial composition of reaction solution				Final pH	Se concentration in filtrate after sorption (mmol/L)
	Selenate (mmol/L)	Selenite (mmol/L)	Na_2CO_3 (mmol/L)	Medium (mmol/L)		
–	9.7×10^{-2}		1	$NaNO_3$, 20	9	1.0×10^{-1}
–	1.0×10^{-2}		1	$NaNO_3$, 20	9.1	1.0×10^{-2}
–		9.6×10^{-2}	1	$NaNO_3$, 20	9.1	9.7×10^{-2}
–		1.0×10^{-2}	1	$NaNO_3$, 20	9.0	9.5×10^{-3}
–		9.7×10^{-4}	1	$NaNO_3$, 20	9.1	1.0×10^{-3}
1	1.0×10^{-2}		1	$NaNO_3$, 20	6.9	1.0×10^{-2}
1	1.0×10^{-2}		1	$NaNO_3$, 20	7.9	1.0×10^{-2}
1	1.0×10^{-2}		1	$NaNO_3$, 20	9.1	9.5×10^{-3} (3 days)[a] 9.4×10^{-3} (5 days)[a] 1.0×10^{-2} (7 days)[a]
1		1.0×10^{-2}	1	$NaNO_3$, 20	9.1	4.1×10^{-4} (3 days)[a] 4.2×10^{-4} (5 days)[a] 3.9×10^{-4} (7 days)[a]
1	9.7×10^{-2}		0.1	$NaNO_3$, 20	9.2	9.7×10^{-2} (microfiltration)[b] 1.0×10^{-1} (ultrafiltration)[b]
1		9.7×10^{-2}	1	$NaNO_3$, 20	9.2	1.8×10^{-2} (microfiltration)[b] 1.8×10^{-2} (ultrafiltration)[b]
1		9.7×10^{-2}	0.1	$NaNO_3$, 20	9.0	1.1×10^{-2} (microfiltration)[b] 1.1×10^{-2} (ultrafiltration)[b]
1	9.7×10^{-2}		–	$NaNO_3$, 20	7.0	9.7×10^{-2}
1	1.0×10^{-2}		–	$NaNO_3$, 20	7.1	9.7×10^{-3}
1	9.7×10^{-2}		–	$NaClO_4$, 20	9.1	1.0×10^{-1}
1	1.0×10^{-2}		–	$NaClO_4$, 20	9.1	9.7×10^{-3}
1		1.0×10^{-1}	–	–	9.1	5.2×10^{-3}
1		9.7×10^{-2}	–	$NaClO_4$, 20	9.1	5.6×10^{-3}
1		1.0×10^{-1}	1	-	9.1	1.6×10^{-2}
1		1.0×10^{-1}	1	$NaClO_4$, 20	9.1	1.7×10^{-2}
1		9.7×10^{-3}	10	$NaNO_3$, 20	9.4	1.6×10^{-3}
1		9.7×10^{-3}	10	$NaClO_4$, 20	9.3	1.1×10^{-3}
1		1.0×10^{-2}	0.1	$NaNO_3$, 20	8.9	2.5×10^{-4}
1		1.0×10^{-2}	0.1	$NaClO_4$, 20	8.7	2.3×10^{-4}

[a] Sorption reaction time.
[b] Sample solution was filtered by a 0.22 μm pore size micro-filter or an NMWL 10 k ultrafiltration membrane.