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Interaction of selenite with reduced Fe and/or S species: An XRD and XAS study

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ABSTRACT

In this study, we investigated the interaction between selenite and either $Fe^{(II)}{}_{aq}$ or $S^{(-II)}{}_{aq}$ in solution, and the results were used to investigate the interaction between $Se^{(IV)}{}_{aq}$ and FeS in suspension. The reaction products were characterized by a combination of methods (SEM, XRD and XAS) and the reaction mechanisms were identified. In a first experiment, $Se^{(IV)}{}_{aq}$ was reduced to $Se^{(0)}$ by interaction with $Fe^{(II)}{}_{aq}$ which was oxidized to $Fe^{(III)}$, but the reaction was only partial. Subsequently, some $Fe^{(III)}$ produced akaganeite (β-FeOOH) and the release of proton during that reaction decreased the pH. The pH decrease changed the Se speciation in solution which hindered further $Se^{(IV)}$ reduction by $Fe^{(II)}{}_{aq}$. In a second experiment, $Se^{(IV)}{}_{aq}$ was quantitatively reduced to $Se^{(0)}$ by $S^{(-II)}{}_{aq}$ and the reaction was fast. Two sulfide species were needed to reduce one $Se^{(IV)}$, and the observed pH increase was due to a proton consumption. For both experiments, experimental results are consistent with expectations based on the oxidation reduction potential of the various species. Upon interaction with FeS, $Se^{(IV)}{}_{aq}$ was reduced to $Se^{(0)}$ and minute amounts of pyrite were detected, a consequence of partial mackinawite oxidation at surface sulfur sites. These results are of prime importance with respect to safe deep disposal of nuclear waste which contains the long-lived radionuclide ^{79}Se. This study shows that after release of $^{79}Se^{(IV)}$ upon nuclear waste matrix corrosion, selenite can be reduced in the near field to low soluble $Se^{(0)}$ by interaction with $Fe^{(II)}{}_{aq}$ and/or $S^{(-II)}{}_{aq}$ species. Because the solubility of $Se^{(0)}$ species is significantly lower than that of $Se^{(IV)}$, selenium will become much less (bio)available and its migration out of deep HLW repositories may be drastically hindered.

1. Introduction

Selenium occurs in nature as trace element and as for many elements, it is an essential nutrient for animals and humans, but is toxic at elevated concentrations (Fernández-Martínez and Charlet, 2009). The chemical speciation and thus the solubility of Se in natural systems depend to a large extent on pH and E_h conditions. Under oxidizing conditions, Se occurs as mobile hexavalent (SeO_4^{2-}) and tetravalent (SeO_3^{2-}) oxyanions, whereas it forms low soluble $Se^{(0)}$ and $Se^{(-II)}$ solids under reducing conditions. The oxidized species also show a higher chemical toxicity (Fernández-Martínez and Charlet, 2009) and are considered more mobile in subsurface environments than the reduced species (Masscheleyn et al., 1990). Additionally, the geochemistry of Se is also largely controlled by that of iron, with which Se is closely affiliated in both oxidizing and reducing environments (Hatten, 1977).

Selenium is also produced in nuclear power plants by fission of ^{235}U. The long-lived and radioactive isotope ^{79}Se (half-life of 3.27×10^5 years (Jörg et al., 2010)) present in the high-level nuclear waste (HLW) is considered one of the dose dominant nuclides in safety assessment calculations. Recent studies showed that selenium is present in tetravalent oxidation state in HLW glass (Dardenne et al., 2015). Upon HLW glass corrosion by groundwater in deep repositories, mobile selenite species may thus be released and possibly

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migrate to the far field. However, reducing conditions are expected to develop in e.g. clay-based repository systems (Gaucher et al., 2006) that may reduce $Se^{(IV)}$ to lower oxidation state(s). The presence of reduced $Fe^{(II)}$ and/or $S^{(-I/-II)}$ species as accessory minerals (e.g., pyrite) also buffers the redox milieu.

Dissolved $Fe^{(II)}_{aq}$ and $S^{(-II)}_{aq}$ are expected to be present in deep disposal sites and may have a capacity to reduce $Se^{(IV)}$ similar to that of $S^{(-II)}$- or $Fe^{(II)}$-containing solids. The contact of groundwater with canisters containing HLW will result in steel corrosion, thereby releasing $Fe^{(II)}_{aq}$ species and producing H_2. Studies showed that $Fe^{(II)}$-bearing solids form as secondary phases upon steel corrosion in the presence of clay or clay pore water and that a significant fraction of $Fe^{(II)}_{aq}$ migrates away from the corroding surface (e.g., (Schlegel et al., 2014)). It was also suggested that this $Fe^{(II)}_{aq}$ fraction could favor reduction and immobilization of redox-sensitive radionuclides. Furthermore, the production of H_2 will also very likely improve the conditions for microbial activity (Libert et al., 2011). Specifically, H_2 will constitute an energetic substrate for anaerobic bacterial communities and strongly stimulate reducing reactions involving e.g., sulfates (Libert et al., 2014). The presence of reduced sulfur species (e.g., $S^{(-II)}$) in repository surroundings is thus very likely. Both ferrous iron and sulfide species may be present in a HLW repository surrounding, and each species can provide electrons to reduce $Se^{(IV)}$, thereby significantly lowering the selenium solubility and thus its migration. Reactions involving only two reacting species, where only one can be oxidized and only one can be reduced, can be investigated in great detail more easily than reactions involving various reduced species. Information obtained by investigating simple systems can subsequently be used to study more complex systems where more than one species (e.g., $Fe^{(II)}$ and $S^{(-II)}$ in FeS) can reduce redox-sensitive elements. Unfortunately, only very few investigations have reported on the interaction of $Se^{(IV)}$ with either $Fe^{(II)}_{aq}$ or $S^{(-II)}_{aq}$.

From a thermodynamic viewpoint, the standard reduction potential of sulfides species are lower than that of selenite species (Table 1), meaning that $S^{(-II)}_{aq}$ can reduce $Se^{(IV)}_{aq}$ in an aqueous phase. For example, two sulfide species, each providing two electrons, are needed to reduce one selenite species to its elemental state. Pettine et al. (2012)) reported rates for the reduction of $Se^{(IV)}$ by sulfide, however without structural characterization (i.e., XRD) of formed solid phases. Depending on the chemical conditions, the formation of selenium sulfide or a mixture of elemental selenium and colloidal sulfur particles has also been reported (Geoffroy and Demopoulos, 2011). Unfortunately, these reported studies have been performed under aerobic conditions, and reduced sulfur species can be readily oxidized by oxygen present in the air. Because anoxic conditions will develop during the evolution of a HLW disposal site, additional studies performed in the absence of oxygen are needed in order to be useful for safety performance calculations.

Table 1
Table of selected aqueous species formal potentials (Cornell and Schwertmann, 1996; Bouroushian, 2010) and protonation constants (Olin et al., 2005).

Half-reaction	Formal potential (V vs S.H.E. at 25 °C)
$SeO_3^{2-} + 6H^+ + 4e^- \Leftrightarrow Se(s) + 3H_2O$	+0.875
$HSeO_3^- + 5H^+ + 4e^- \Leftrightarrow Se(s) + 3H_2O$	+0.778
$Fe^{3+} + e^- \Leftrightarrow Fe^{2+}$	+0.770
$H_2SeO_3 + 4H^+ + 4e^- \Leftrightarrow Se(s) + 3H_2O$	+0.740
$S(s) + 2H^+ + 2e^- \Leftrightarrow H_2S(aq)$	+0.141
$S(s) + H^+ + 2e^- \Leftrightarrow HS^-$	−0.065
$S(s) + H_2O + 2e^- \Leftrightarrow HS^- + OH^-$	−0.52
$S(s) + 2e^- \Leftrightarrow S^{2-}$	Available values range from −0.45 to −0.58 V, most probable close to −0.48 V.
Protonation reaction	Protonation constant
$SeO_3^{2-} + H^+ \Leftrightarrow HSeO_3^-$	$\log_{10} K^0 = 8.36 \pm 0.23$
$HSeO_3^- + H^+ \Leftrightarrow H_2SeO_3$	$\log_{10} K^0 = 2.64 \pm 0.14$

The reduction of $Se^{(IV)}_{aq}$ by $Fe^{(II)}_{aq}$ species is more complex. The standard reduction potential of the $Fe^{(III)}/Fe^{(II)}$ couple is higher than that of sulfide (Table 1) and of comparable value than that of the $Se^{(IV)}$ species. The ability of $Fe^{(II)}$ to reduce $Se^{(IV)}$ is governed by the speciation in solution. For example, $HSeO_3^-$ can be reduced by $Fe^{(II)}$ but H_2SeO_3 cannot because of its lower reduction potential. Also, four electrons are needed to reduce one selenite species, i.e., four $Fe^{(II)}$ species must each provide one electron for the reduction of one $Se^{(IV)}$ species. The likelihood of such five species in close proximity in solution in the absence of any mineral surface may be low and if the reaction occurs, it may rapidly slow down because the $Fe^{(II)}_{aq}$ concentration decreases four times faster than that of $Se^{(IV)}_{aq}$. In fact, the ability of $Fe^{(II)}_{aq}$ to reduce $Se^{(IV)}_{aq}$ was questioned by several authors. For example, Chen et al. (2009)) failed to reduce $Se^{(IV)}_{aq}$ by ferrous iron in the absence of reactive surface even though $Fe^{(II)}_{aq}$ was in large excess at $pH < 5.6$. Similarly, Charlet et al. (2007)) failed to reduce $Se^{(IV)}$ but observed the formation of $FeSeO_3$ by mixing $Se^{(IV)}_{aq}$ and $Fe^{(II)}_{aq}$ with a molar ratio of 1:1 at pH 5. The formed solid phase was poorly crystalline (no diffraction data shown); Mossbauer data indicated that half of $Fe^{(II)}$ was oxidized and based on XAS data ~25% Se was reduced after 4 h. Spectroscopic data were consistent with the formation of a nanoparticulate precipitate where surface Fe atoms are oxidized while Se atoms remain 4-fold coordinated by oxygen atoms as is typical for selenite. In these studies, the presence of a mineral surface acted like a catalyzer, meaning that $Se^{(IV)}$ was reduced to $Se^{(0)}$ in the presence of either iron oxides (Chen et al., 2009) or the clay mineral montmorillonite (Charlet et al., 2007). In the present study, the reactivity of $Se^{(IV)}$ in the presence of a large excess of $Fe^{(II)}$ (Fe:Se molar ratio of 4:1) was investigated under anoxic conditions and in the absence of mineral phases.

At ambient temperature and pressure, mackinawite (FeS) is the primary precipitate formed by reaction between $Fe^{(II)}_{aq}$ and $S^{(-II)}_{aq}$ (Rickard et al., 2006). Mackinawite is a highly reactive phase and was used as a substrate in adsorption studies of various actinides such as $Np^{(V)}$ (Moyes et al., 2002) or $Pu^{(V)}$ (Kirsch et al., 2011). Studies on the interaction of $Se^{(IV)}$ with mackinawite have also been reported (Scheinost and Charlet, 2008; Scheinost et al., 2008) and indicated an influence of the chemical conditions on the nature of the formed Se species. However, in these experiments, the contact time was at maximum 1 day and for such rather short contact times kinetically slow reactions can be easily overlooked. In the present study, $Se^{(IV)}$ was contacted with pre-formed mackinawite in suspension for several days before spectroscopic analysis of the sample.