

Reduction of selenite on iron surfaces: A micro-spectroscopic study

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Abstract. Under anoxic conditions zero-valent iron can react with water to produce hydrogen gas and magnetite or green rust, a highly reactive mineral phase that can induce reduction processes and thus control the speciation, the solubility, toxicity and the mobility of redox sensitive elements in (nuclear) waste repositories. In this study micro X-ray fluorescence (micro-XRF) and micro X-ray absorption spectroscopy (micro-XAS) were used to investigate the speciation of selenium that immobilized in the presence of Fe(0) and an anoxic synthetic groundwater solution. The selenium immobilization was accompanied by the formation of a green rust corrosion layer. Micro-XRF revealed that a Se-rich layer is present along the iron surfaces that were exposed to the Se(IV) solution. Micro-XAS experiments at the Se K-edge showed that Se(IV) was reduced to elemental Se(0). Thus, the reactivity of zero-valent and green rust should be considered in assessing the long-term fate of selenium in nuclear waste repositories.

1. INTRODUCTION

In deep nuclear waste repositories, significant amounts of iron and steel will be present in various waste types, e.g., “hulls and ends” produced during reprocessing of spent fuel, canisters for high-level glass wastes and spent fuel, parts of decommissioned nuclear power plants, and – in the caverns – as reinforcement steel. In nuclear safety assessment it is assumed that ground water will break through the engineered barrier systems (clay and cement) and corrode the waste canisters leading to canister breaching within timeframes of >1000 years. Under anoxic conditions (deep ground-waters are oxygen free) iron can then react with water to produce hydrogen gas and magnetite. Further corrosion product that may be formed are or Fe(II)-Fe(III)-hydroxy compounds [1]. Fe(II)-Fe(III)-hydroxy compounds are known as green rusts and are characterized by a layered structure made of brucite-like sheets, positively charged due to the trivalent Fe cations, $[\text{FeII}_{(1-x)}\text{FeIII}_x(\text{OH})_2]^{x+}$, which alternate with interlayers composed of anions (e.g., CO_3^{2-} , Cl^- , SO_4^{2-}) restoring the overall electroneutrality and water molecules [2].

It has been shown that green rust is a highly reactive mineral phase in geochemical setting such as soils, sediments, and aquifers. Under anoxic conditions, it favors reduction processes and thus may control the speciation, the solubility, the bioavailability, the toxicity and the mobility of redox sensitive elements (e.g., Se, Cr, U, Pu, Np, Tc,) in natural environments. A recent study on the corrosion of iron insert in contact with ground waters has demonstrated that after a reaction time of 3 months an uneven few micron thick layer of carbonate green rust ($\text{Fe(II)}_4\text{Fe(III)}_2(\text{OH})_{12}\text{CO}_3$) is formed on the surface of the iron insert [3]. In addition, it was noticed that U(VI) was reduced to U(IV) and some UO_2 crystals (3-5 μm sized) formed on top of the carbonate green rust layer were observed. This finding demonstrates the ability of Fe(0) and/or green rust to reduce U(VI) and suggests that other redox sensitive inorganic contaminants or radionuclides can be reduced in the presence of zero-valent iron and/or a green rust corrosion layer.

To test this hypothesis with selenium (⁷⁹Se corresponds to a long-lived fission product in radioactive waste), non-radioactive Se(IV) was immobilized by Fe(0) and /or a green rust corrosion layer that formed

in the presence of a synthetic groundwater solution on the iron surface. Micro-XRF and micro-XAS were used to obtain spatially resolved information on the oxidation state and structural coordination of Se in the Fe(0)/green rust system.

2. METHODS AND RESULTS

Batch experiments were conducted in glass bottles in an atmosphere (Ar +0.03% CO₂) controlled vessel. An in-situ oxygen trap was used as described in [3]. An Fe(0) foil, 99.99% purity and 7×20×0.5 mm³ in size, was contacted with a synthetic groundwater (10 mM NaCl, 2 mM NaHCO₃, pH = 8.5) and a Se(IV) containing solution ([Se] = 6.3 10⁻⁵ M) for three months. The solution analysis showed that almost all Se(IV) disappeared from solution within the first 8 days.

A part of the corrosion products on the iron foil was peeled under Ar atmosphere and analyzed by powder X-ray diffraction (XRD). The remaining part of the corroded iron foil was cut, embedded in an epoxy resin, polished, and coated with a thin Au layer for scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) investigations. XRD measurements revealed diffraction lines characteristic for the presence of the green rust phase Fe(II)₄Fe(III)₂(OH)₁₂CO₃. Furthermore, by using SEM-EDS, a several micrometer thick Se-containing corrosion layer was observed on the iron foil corroded in Se(IV) solution. The results of solution and surface analysis will be discussed and reported in detail separately [4]. Micro-XRF and Se K-edge (12.6 keV) micro-XAS experiments on the Se(IV) treated iron foil were performed at the ALS beamline 10.3.2, a bending magnet beamline dedicated to microXAS. The measurements were conducted using Si(111) monochromator crystals, a pre-focusing mirror and a pair of Kirpatrick-Beaz (KB) mirrors. The beamsize used for this study was ~ 15 x 10 μm². EXAFS data reduction was performed using WinXAS 2.3 following standard procedures [5]. Theoretical scattering paths for the fit were calculated with FEFF 8.02 [6], using the structures of elemental Se [7].

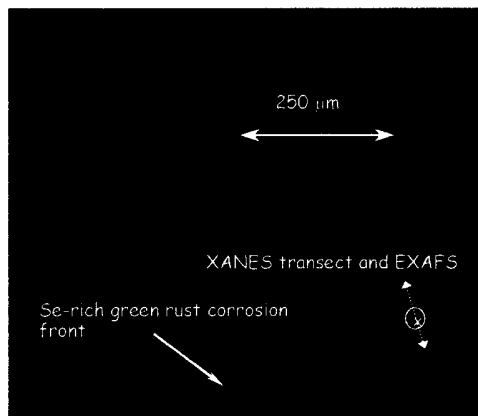


Figure 1. XRF map (at 13 keV) of a horizontally cut ~500 micron thick metallic Fe foil. The iron surfaces exposed to an anoxic Se(IV) solution are shown in the lower part of the image. Se is represented in red and Fe in blue. The bottom part of the fluorescence map exhibits shadowing artefacts.

Figure 1 shows an XRF map of a metallic Fe foil. The mapping revealed that a Se rich layer (bright red, up to 15 micron thick) is present along iron surfaces that were exposed to the Se(IV) solution. This finding clearly suggests that selenium does interact with the green rust corrosion layer. In a next step vertical Se K-edge XANES (X-ray absorption near edge structure) spectra across the corrosion layer were performed. The XANES data revealed that E_0 (taken as half step height of normalized spectra) shows a minor shift to lower energies when scanning from the outer side of the sample through the corrosion layer into the iron foil (Figure 2). Furthermore, we observed changes in the position and in the relative intensity of the white line and the first oscillation, possibly suggesting the presence of different Se species across the corrosion layer. However, a comparison with reference compounds (ZnSe, Se(IV)O₃²⁻ solution,

Se(VI)O_4^{2-} solution, [data collected at the European Synchrotron Radiation Facility ESRF, Grenoble, France]) clearly illustrates that Se(IV) was reduced at the green rust layer and that the edge position is roughly in line with the inter-metallic form of Se found in ZnSe.

In order to gain information on the speciation and coordination environment of Se within the corrosion layer, we performed EXAFS (extended X-ray absorption fine structure) measurements on a Se rich spot (see Fig. 1). The EXAFS spectrum shows – in a first approximation – a single backscattering envelope with its maximum at high k (around 9 \AA^{-1}), which is characteristic of the presence of heavy backscattering atoms (Figure 3a). The Fourier transform is depicted in Figure 3b and shows a single RSF peak at $R + \Delta R = \sim 2.1 \text{ \AA}$. Data analysis revealed ~ 3 Se neighbors at $\sim 2.34 \text{ \AA}$ (fits are represented as dashed lines in Figure 3a and Figure 3b). Such a bond distance is much longer than the initial Se-O distances in Se(IV)O_3^{2-} ($\sim 1.70 \text{ \AA}$) but close to typical Se-Se distances observed in elemental selenium ($R_{\text{Se-Se}} = \sim 2.30 \text{ \AA}$). This finding suggests that Se(IV) did undergo reduction to Se(0) .

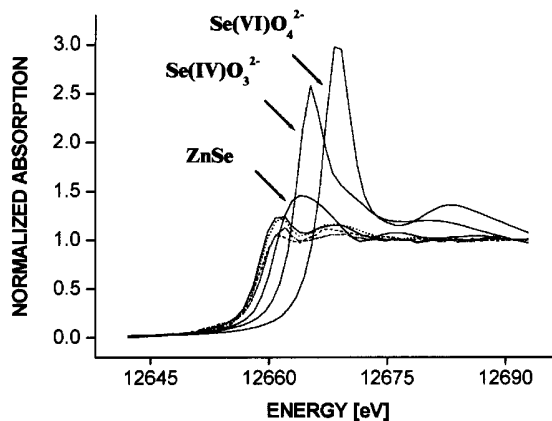


Figure 2. XANES spectra collected along a vertical line scan from the outer side of the sample through the corrosion layer into the iron foil (Sequence: solid, dotted, dashed, dashed-dotted).

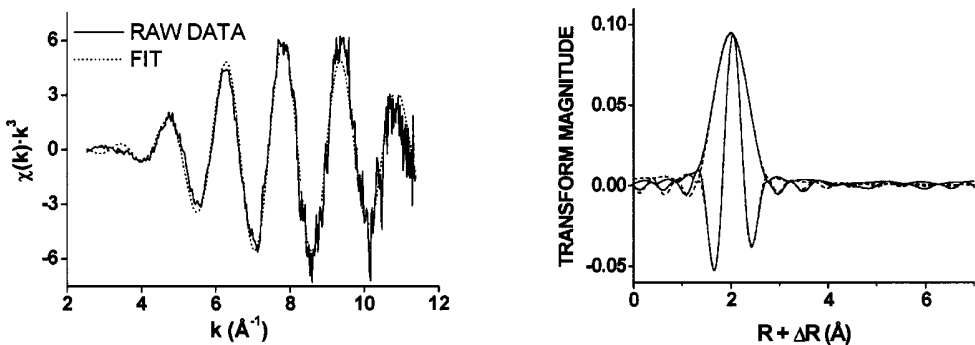


Figure 3. a) k^3 -weighted Se K-edge EXAFS spectrum and b) Fourier transform (modulus and imaginary parts). Solid lines: experimental data, dotted line: least square fit.

3. DISCUSSION

The micro-spectroscopic findings presented in this study clearly demonstrate that the corrosion of zero-valent iron to green rust can reduce Se(IV)O_3^{2-} to elemental Se(0) within a time frame of <3 months. This finding coincides with the results of a study on abiotic selenium redox transformations in the presence of green rust [8]. Using bulk XAS the authors [8] observed that Se(IV)O_4^{2-} was reduced to Se(O) in the presence of green rust formed from a Fe(II) solution. When Se(VI) was present during green rust precipitation, the reduction kinetics to Se(0) was fast (<150 hours) and depended on pH conditions (faster at alkaline than at near-neutral conditions). Interestingly, at near-neutral conditions, an intermediate Se(IV) species could be observed. In another study [9] XPS and Mössbauer spectroscopy was used to study the reduction of Se(VI) by green rust, again formed from a Fe(II) solution. These experiments, however, were performed under oxic conditions. Under such conditions, the reduction of Se(VI) to Se(0) did not occur and an equal amount of the selenium was either present as Se(IV) species or incorporated as Se(VI) species into the green rust interlayers.

In geochemical settings selenium can occur in VI, IV, 0 and -II oxidation states. The higher valent Se forms (VI and IV) are present as oxyanions and considered to be more soluble and more mobile. The reduced Se species (0 and -II) are either precipitates, or strongly bound to mineral surfaces. The present study demonstrates that the corrosion of Fe(0) to green rust can reduce selenium and thus impact the speciation and mobility of radionuclides in nuclear waste repositories. Thus, the reactivity of green rust should to be considered in assessing the long-term fate of selenium and redox-sensitive radionuclides in nuclear waste repositories.

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