Micro-spectroscopic study on the reduction of selenite on iron(0) surfaces

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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 Fe(II)-Fe(III)-hydroxy compounds known as green rusts [1]. Green rust species are highly reactive mineral phases in geochemical setting such as soils, sediments, and aquifers. Under anoxic conditions, these iron phases favor reduction processes and thus may control speciation, solubility, bioavailability, toxicity, and mobility of redox sensitive elements (e.g., Se, Cr, U, Pu, Np, Tc,) in natural and engineered environments. In this study 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 (the unstable ^{79}Se corresponds to a long-lived fission product in radioactive waste). 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.

RESULTS AND DISCUSSION

An Fe(0) foil (99.99% purity) was contacted for three months with a synthetic groundwater (10 mM NaCl, 2 mM NaHCO$_3$, pH = 8.5) containing Se(IV) (with [Se] = 6.3 10^{-5} M). The experiments were conducted in a controlled atmosphere (99.97% Ar, 0.03% CO$_2$) [2]. The corroded iron foil was cut, embedded in an epoxy resin, polished, and the polished area was coated with a thin Au layer for further investigations. XRD measurements revealed diffraction lines characteristic for the presence of the green rust phase Fe(II)$_4$Fe(III)$_2$(OH)$_{12}$CO$_3$. By using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS), a several micrometer thick Se-containing corrosion layer was observed on the iron foil exposed to the Se(IV) solution. 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 [3]. The measurements were conducted using Si(111) monochromator crystals, the 1:1 pre-focusing mirror and a pair of Kirkpartrick-Baez (KB) mirrors. The beamsize used for this study was ~ 15 x 10 μm^2.

Figure 1 shows a XRF map of the sliced metallic Fe foil. The mapping revealed that a Se rich layer (red to bright yellow, up to 15 micron thick) is present along iron surfaces that were exposed to the Se(IV) solution. This finding suggests that either selenium does interact with the green rust corrosion layer or selenium is actively involved in the formation processes of this corrosion product. 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). We also 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. Furthermore, a comparison with reference compounds (elemental Se(0), Se(IV)O_3^{2-} solution, Se(VI)O_4^{2-} solution, [4]) clearly illustrates that Se(IV) was reduced within the green rust layer and that the edge position is roughly in line with elemental selenium.
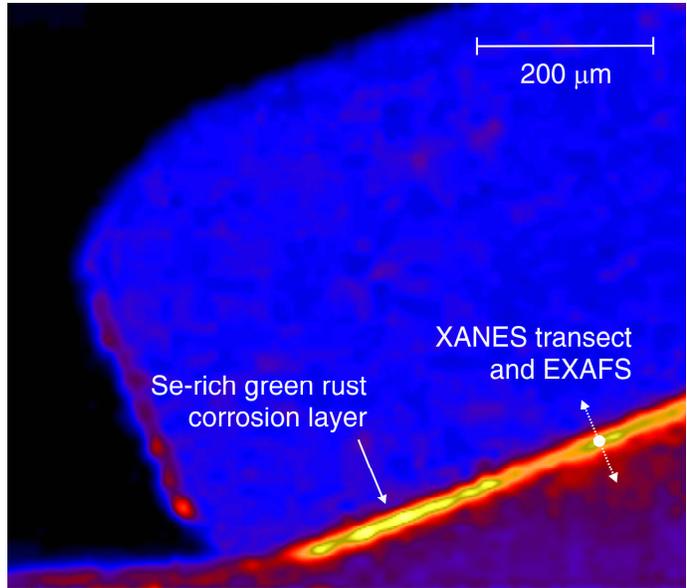
Figure 1. XRF map (at 13 keV) of a horizontally cut ~500 micron thick metallic Fe foil. The iron surfaces exposed to an anoxic Se(IV) solution are shown in the lower part of the image. Se is represented in red-to-yellow and Fe in blue. The bottom part of the fluorescence map is partly impaired by experimental and instrumental artefacts.

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 Figure 1) [5]. The EXAFS spectrum shows – in a first approximation – a single backscattering envelope with its maximum at high k (around 9Å^{-1}), which is characteristic of the presence of heavy back-scattering atoms (Figure 3a). The Fourier transform is depicted in Figure 3b and shows a single RSF peak at R+ΔR = ~2.1 Å. Data analysis revealed ~3 Se neighbors at ~2.34 Å (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-} (~1.70 Å) but close to

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: blue, red, green, yellow).

typical Se-Se distances observed in elemental selenium. 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 with valency (0) or (–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.
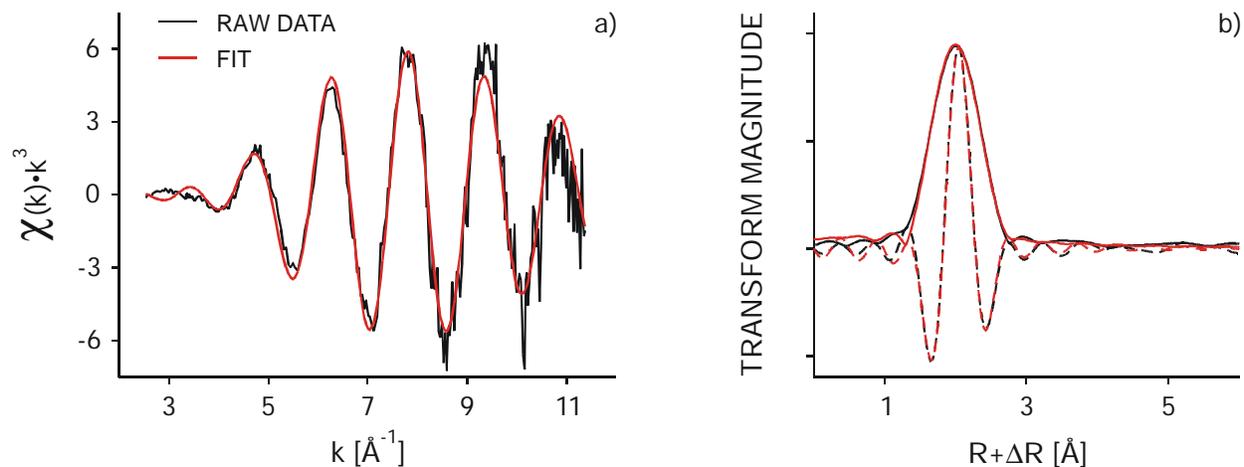
Figure 3. a) k^3-weighted Se K-edge EXAFS spectrum and b) Fourier transform (modulus and imaginary parts). Black lines: experimental data, red lines: least square fit.

References

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