Electron transfer during selenium reduction by iron surfaces in aqueous solution: high resolution X-ray absorption study

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Abstract. We present a study of selenate (SeO$_4^{2-}$) on an iron surface in ground water solution by X-ray absorption near-edge spectroscopy. Spectral sharpening is obtained by using the high energy resolution fluorescence detection technique that also efficiently suppresses the strong fluorescence signal from the Fe surface in the highly dilute samples (Se concentration < 3 ppm). We observe fully reduced Se on polished Fe surfaces while no changes are found for Se on oxidized Fe surface.

1. Introduction

During the coming decades, one of the largest challenges facing the world is stabilization and immobilization of nuclear waste. Recent safety evaluation has demonstrated that $^{79}$Se radionuclides could contribute significantly to the dose released during the next million years \cite{1}. The fraction of selenium is comparably small at ~ 0.04\% of the fuel at the time of discharge. However the long half life of $^{79}$Se (1.1 million years) combined with potentially high mobility makes selenium one of the key concerns of the safety assessment for a waste repository system.

As a redox sensitive element, selenium can exist in four different oxidation states. Elemental selenium Se(0) and metal-selenide minerals (like FeSe$_2$) are stable and poorly soluble. Tetravalent Se (IV) is a stable valence state under anoxic conditions and can exist as the selenite (SeO$_3^{2-}$) anion, which can be bound to a metal surface (if they are present in the local environment). Under oxidizing conditions, the Se (VI) valence state is the dominant species and exists as the selenate (SeO$_4^{2-}$) anion which shows high mobility in soils and ground water \cite{2-6} . Depending on the pH conditions, the selenate anion can reach high concentrations due to increased solubility. It is therefore important to study the behavior of selenate in the framework of radioactive waste disposal.

Several suggestions for encapsulating nuclear waste mainly rely on geological isolation in order to prevent the radionuclides reaching the biosphere. In most designs a significant part of the disposal
canisters placed underground contains iron or steel carbon inserts [7]. The inner part will come into contact with anoxic circulating ground water, which can corrode the canister and release fission products [8]. In order to improve the safety of these canisters, relevant information on selenium species in a ground water environment in contact with a metal surface should be investigated.

In the present paper the electronic structure of selenium on different iron surfaces previously exposed to a ground water solution was probed by X-ray absorption near edge spectroscopy (XANES). Selenium K-edge XANES was used to study selenium behavior on pre-oxidized and polished iron surfaces. The extraction of information is based on the fingerprint approach where the comparison of XANES spectra with model systems is used in the interpretation and analyses.

2. Experimental details

The experiments were performed at beamline ID26 at the European Synchrotron Radiation Facility [9]. The incident energy was selected using the <111> reflection from a double Si crystal monochromator. Rejection of higher harmonics was achieved by Si mirrors with a Pd/Cr layer working under total reflection. XANES spectra were measured by total fluorescence yield (TFY) using a photodiode, and in high energy resolution fluorescence detection (HERFD) mode using an X-ray emission spectrometer [10]. The Se HERFD spectra at the K-edge were obtained by recording the intensity of the Se Kα1 emission line (11224 eV) as a function of the incident energy. The emission energy was selected using the <844> reflection of a spherically bent Si crystal analyser aligned at 85° Bragg angle. A combined (incident convoluted with emitted) energy resolution of 1.9 eV was obtained as determined by measuring the elastic peak. The presented data is not corrected for self-absorption effects. The analysis showed in this work is based on comparison of the energy position of the main Se K-edge white line which is only little affected by self-absorption effects.

For spectroscopic investigations two types of material were prepared. A steel carbon foil was cut inside a glovebox (O₂ level < 0.1 ppm), polished with sand paper and exposed to the ground water with selenate solution for 5.5 months. A second iron sample was pre-corroded in heated water at 90°C and air saturated neutral distilled water for 4 weeks, divided into several small pieces and then exposed to the ground water solution [11]. The selenium concentrations in both solutions were found to be ~ 3 ppm at the start and end of exposure. The samples were then removed from the solution, briefly dipped in deionised water, then ethanol, and dried. Solid samples were sealed in a custom transportation box and safely transported to the beamline. Solid iron samples containing Se were placed at the sample stage one hour before XANES data were recorded. These samples did not appear to be sensitive to oxidation in air or to radiation damage during the X-ray exposure.

3. Results and discussions

Figure 1 shows the Se K-edge XANES spectra of Se samples on Fe foils (labelled as “Se on polished Fe” and “Se on oxidized Fe”) and five reference materials. Due to dipole selection rules at the Se K-edge, electrons are from the 1s core level being excited into unoccupied 4p states. For the model systems, clear shifts of the white line can be distinguished. The edge position shifts to lower energy with decreasing oxidation state due to a less efficient screening of the nuclear charge by the valence electrons. [2-6]

XANES in both HERFD and TFY mode were recorded simultaneously. However in the HERFD setup, only emission from the Se Kα1 line reaches the detector and an excellent signal-to-noise ratio is achieved (a comparison between TFY and HERFD signal is shown on Figure 1 for Na₂SeO₃). In a conventional setup using a solid state detector the total signal from Se on iron samples would be dominated by the Fe fluorescence, and at high count rates the detector response would become non-linear. The count rate in the HERFD signal of a sample with < 3ppm of Se is ~ 23000 counts/sec at 50 eV above the Se edge. This allows XANES spectra to be collected in a reasonable time (10 minutes/scan). We note that HERFD-XANES does not necessarily measure the absorption cross...
In this study we only discuss HERFD data that were all recorded on the maximum of the Se K\(\alpha_1\) line. The identical experimental protocol ensures that the comparison between the HERFD data is consistent. Furthermore, final state effects that would cause strong deviations in HERFD from the absorption cross section are expected to be weak in Se because of the delocalization of the 4p orbitals.

![Figure 1](image)

**Figure 1.** High energy resolution fluorescence spectra of FeSe, elemental black and red selenium, \(\text{Na}_2\text{SeO}_3\), \(\text{Na}_2\text{SeO}_4\), and two iron films exposed to the ground water solution with selenate ions. The spectra were recorded by means of an X-ray emission spectrometer with its detector tuned to the Se K\(\alpha_1\) emission line.

We observe an energy shift of 7.95 eV of the main Se white line between oxidized and polished Fe surfaces in HERFD-XANES spectra. Comparison with Se model systems shows that Se is reduced only on the polished Fe surface and remains as Se(VI) on the oxidized Fe surface. This can be readily explained by the presence of an already positively charged Fe ion that does not allow for Se reduction. Selenium thus remains chemically unaltered and the spectrum corresponds to \(\text{Na}_2\text{SeO}_4\) as the starting material. The peak position in the spectrum of Se on polished Fe nearly overlaps with the peak of the reference FeSe sample. The good agreement between these spectra suggests that Se on the polished Fe surface is fully reduced to Se(II-) and is most likely in the form of iron selenide.
4. Conclusions

We have shown that Se is reduced to Se(II-) in the presence of a polished Fe surface in ground water. Selenium remains chemically unchanged on an oxidized Fe surface. Excellent data quality was achieved by applying the HERFD-XANES where the fluorescence is monochromatized by Bragg reflection from a perfect Si crystal. The Fe fluorescence is thus eliminated and linear detector response can easily be achieved. These results suggest that the degree of iron oxidation in nuclear waste disposal canisters may have an important influence on the release of selenium into the environment.

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