



	<b>Experiment title:</b> EXAFS investigations of Se uptake by layered double hydroxides (AFm phases) in hardened cement paste under oxidizing and reducing conditions.	<b>Experiment number:</b> EV-39
<b>Beamline:</b> BM 20	<b>Date of experiment:</b> from: 30/09/2013 to: 05/10/2013	<b>Date of report:</b> 28.02.2014
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## Report:

Cementitious materials play a crucial role in the engineered barrier system in repositories for low and intermediate level radioactive waste (L/ILW). This type of nuclear waste contains significant amounts of the fission product <sup>79</sup>Se. <sup>79</sup>Se is of concern in waste disposal due to its long half-life ( $3.27 \cdot 10^5$  years), its presence as weakly sorbing anionic species under oxidizing conditions ( $\text{Se}^{\text{IV}}\text{O}_3^{2-}$ ) and its complex speciation under reducing conditions ( $\text{Se}^0$ , polymeric Se species and  $\text{Se}^{\text{II}}$ ). Predicting its long-term mobility requires a thorough understanding of the processes controlling the <sup>79</sup>Se sorption onto cementitious materials. The aim of the project was to assess the sorption of  $\text{Se}^{\text{IV}}$  and  $\text{Se}^{\text{II}}$  onto anion exchangers such as AFm phases in cement, and to assess the fate of these sorbed anions upon changes of the redox potential.

## Preliminary results:

Se K-edge (12.6 keV) extended X-ray absorption fine structure (EXAFS) measurements were performed on wet pastes of AFm-CO<sub>3</sub> and AFm-OH-CO<sub>3</sub> doped with ~1000 ppm of either  $\text{Se}^{\text{IV}}\text{O}_3^{2-}$  or  $\text{HSe}^{\text{II}}$ . All samples were equilibrated for 30 days. After this equilibration time, part of the  $\text{Se}^{\text{IV}}$  doped samples were exposed to reducing conditions either electrochemically ( $E_h = -1.285$  V (SHE)) or through the addition of 0.05 M hydrazine for 30 more days. Thermodynamic calculations showed that the Se concentrations used in the sorption experiments were sufficiently low to avoid undesired precipitation of  $\text{CaSeO}_3$  and insoluble selenides. A  $\text{Se}^{\text{II}}$  solution was prepared electrochemically and the Se redox state verified with UV-Vis spectroscopy. All experiments were conducted inside a glovebox ( $[\text{CO}_2], [\text{O}_2] < 0.1$  ppm). All samples (wet pastes) and solid reference compounds were packed in plexiglass sample holders and sealed with Kapton tape. The reference solutions were kept in sealed Pasteur pipettes. In order to avoid oxidation during transport, all samples were stored in a dewar under liquid N<sub>2</sub> conditions.

The EXAFS measurements were conducted at a temperature of 15 K using a closed-loop He-cryostat to avoid oxidation of the  $\text{Se}^{\text{II}}$  samples during measurements and to improve the signal-to-noise ratio by reducing thermal disorder effects. EXAFS data were analyzed and fitted using WINXAS and IFEFFIT software package. Theoretical scattering paths were calculated with FEFF8.2, including multiple scattering paths.

Figure 1 shows XANES spectra of  $\text{Se}^{\text{IV}}$  sorbed on AFm-CO<sub>3</sub> and AFm-OH-CO<sub>3</sub> phases, equilibrated for 30 days followed by exposure to reducing conditions for 30 more days established either electrochemically or by addition of 0.05 M hydrazine. The spectra are compared with spectra of a  $\text{Se}^{\text{IV}}$  reference ( $\text{Na}_2\text{SeO}_3$ ), and an aqueous  $\text{Se}^{\text{II}}$  reference (a  $\text{NaHSe}$  solution, pH = 12.0). The figure shows clearly that the XANES spectrum of the sample corresponding to  $\text{Se}^{\text{IV}}$  sorbed on AFm-CO<sub>3</sub> followed by equilibration for 30 days under reducing conditions in an electrochemical cell, is very similar to the  $\text{Se}^{\text{II}}$  reference spectrum and completely different

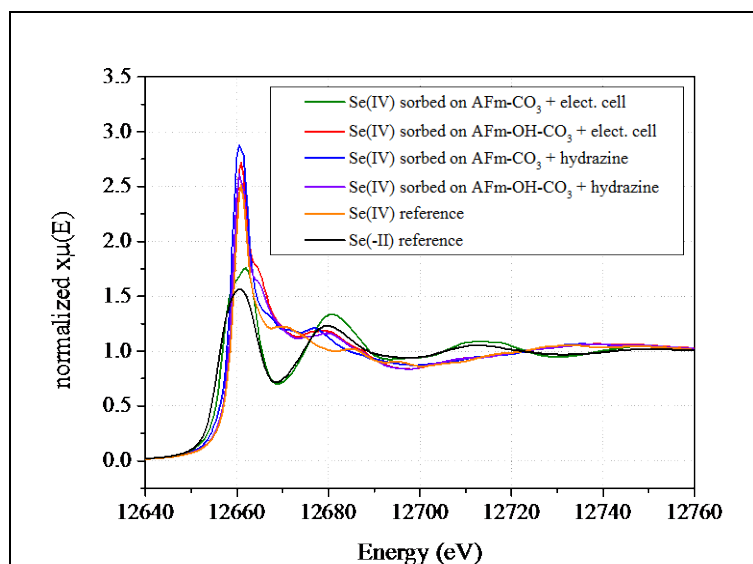


Fig. 1. spectra of samples with Se(IV) sorbed on AFm phases and applying reducing conditions established either electrochemically or by addition of hydrazine. Comparison with XANES spectra of a Se(-II) reference solution sample and  $\text{Na}_2\text{Se(IV)O}_3$  reference sample.

from the spectra of the other samples. Two conclusions can be drawn from these results:

1)  $\text{Se}^{\text{IV}}$  sorbed onto AFm- $\text{CO}_3$  cannot be reduced within 30 days in contrast to  $\text{Se}^{\text{IV}}$  sorbed onto AFm-OH- $\text{CO}_3$ . This may be an indication for different sorption mechanisms acting on the two solids. 2) Hydrazine cannot reduce sorbed  $\text{Se}^{\text{IV}}$  although it is capable of reducing  $\text{Se}^{\text{IV}}$  in solution.

Fig. 2 shows the Fourier transform (FT) spectra of  $\text{Se}^{\text{IV}}$  (a) and  $\text{Se}^{\text{-II}}$  (b) loaded AFm- $\text{CO}_3$  and AFm-OH- $\text{CO}_3$  phases. The FT spectrum corresponding to Se(IV) sorbed on AFm-OH- $\text{CO}_3$  phase reveals the absence of backscattering contributions beyond the oxygen shell indicating the formation of an outer-sphere complex. In the case of  $\text{Se}^{\text{IV}}$  sorbed on AFm- $\text{CO}_3$ , however, backscattering contributions from three shells beyond the oxygen shell are observed in the FT spectrum suggesting the formation of a  $\text{Se}^{\text{IV}}$  precipitate. In the case of the  $\text{Se}^{\text{-II}}$  loaded AFm- $\text{CO}_3$  and AFm-OH- $\text{CO}_3$

samples, both spectra exhibit very similar shapes characterized by a very rich structure hinting at the formation of a  $\text{Se}^{\text{-II}}$  secondary phase.

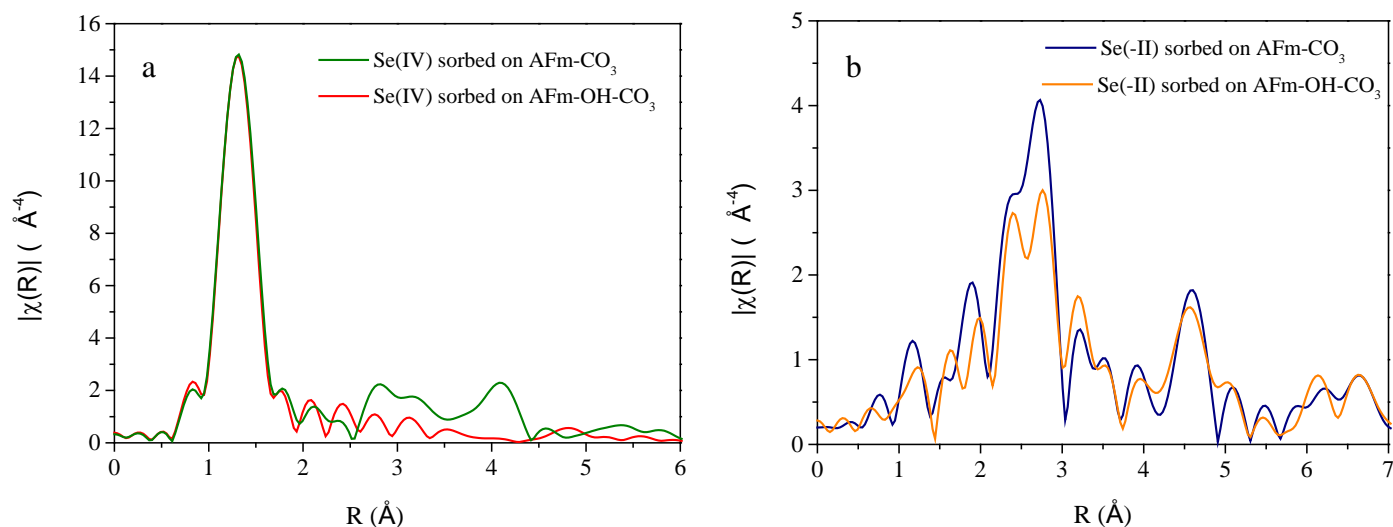


Fig. 2. Fourier transform spectra of Se(IV) (a) and Se(-II) (b) on AFm- $\text{CO}_3$  and AFm-OH- $\text{CO}_3$  phases.

### Future Outlook:

To complete this study, some additional XAS measurements are planned focussing on the measurement of  $\text{Se}^{\text{IV}}$  and  $\text{Se}^{\text{-II}}$  reference samples ( $\text{CaSeO}_3$ ,  $\text{Na}_2\text{SeO}_3$ ,  $\text{Na}_2\text{Se}$ ), as well as AFm- $\text{CO}_3$  and AFm-OH- $\text{CO}_3$  samples with lower loading of  $\text{Se}^{\text{IV}}$  and  $\text{Se}^{\text{-II}}$  in an effort to avoid surface precipitation.

### Conferences contributions:

- “Retention of selenium by cementitious materials under reducing radioactive waste repository conditions”, **Rojo H., Tits J., Scheinost A.C., Wieland E.** Goldschmidt 2014 conference, 8-13 June, 2014, Sacramento, California. Poster.
- “Retention of selenium by cementitious materials under anoxic and reducing conditions”, **Rojo H., Tits J., Scheinost A.C., Wieland E.** IGDTP - Geodisposal 2014 conference, 24-26 June, 2014, Manchester. Poster.