 ROBL-CRG	Experiment title: EXAFS investigations of Se uptake by layered double hydroxides (AFm phases) in hardened cement paste under oxidizing and reducing conditions.	Experiment number: 20-01-729
Beamline: BM 20	Date of experiment: from: 12/07/2013 to: 22/02/2014	Date of report: 07.02.2017
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Background and objectives:

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 ⁷⁹Se. ⁷⁹Se 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 (Se^0 , polymeric Se species and Se^{II}). The aim of the project was to assess the sorption of Se^{IV} and Se^{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. This study is a continuation of an earlier EXAFS study carried out at the ROBL beamline, BM20 at ESRF (EV-39). Fourier transform (FT) spectra obtained in this first study suggested the formation of Se surface precipitates in part of the samples. In the present campaign sample preparation was optimized to avoid oversaturation w.r.t CaSeO_3 . Furthermore, the fate of Se^{IV} and Se^{II} sorbed onto AFm phases upon changes of the redox potential, was investigated in more detail.

Sample preparation and XAS measurements:

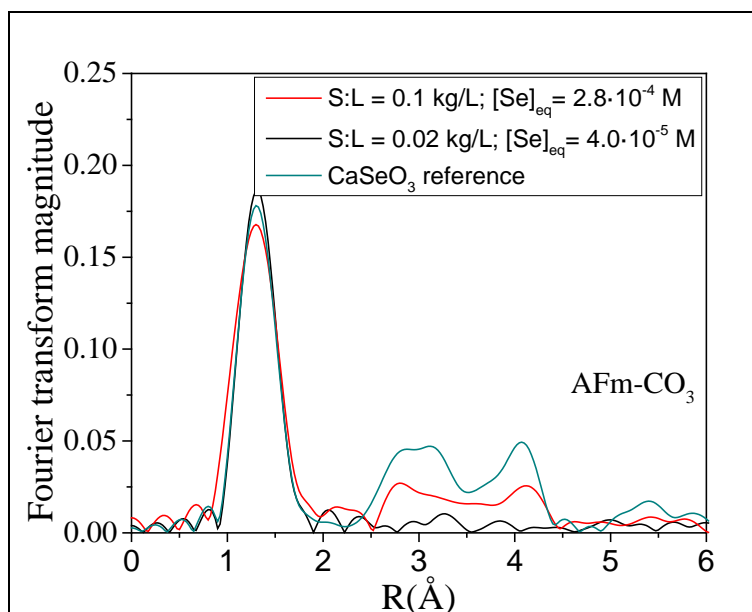


Fig. 1. FT spectra of AFm-CO₃ loaded with 1000 ppm Se^{IV} using two S:L ratios. Comparison with the FT spectrum of a CaSeO₃ reference

Se K-edge (12.6 keV) extended X-ray absorption fine structure (EXAFS) measurements were performed on wet pastes of AFm-CO₃ and AFm-OH-CO₃ doped with ~1000 ppm of either $\text{Se}^{\text{IV}}\text{O}_3^{2-}$ or HSe^- . The Se^{II} solution required for the preparation of the Se^{II} loaded samples was prepared electrochemically. Variation of the S:L ratio of the AFm suspensions allowed to vary $[\text{Se}]_{\text{tot}}$ in the sorption tests while keeping the Se loading on the solid constant with the aim to reduce the risk of CaSeO_3 or CaSe precipitation. All samples were equilibrated for 30 days. After this equilibration time, part of the Se^{II} doped samples were briefly exposed to air to allow oxidation of sorbed Se^{II} . Part of the Se^{II} doped samples were briefly exposed to air prior to XAS sample preparation. 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 N₂ conditions. The EXAFS measurements were conducted at a temperature of 15 K using a closed-loop He-cryostat to avoid oxidation of the Se^{II} samples during measurements and to improve the signal-to-noise ratio by reducing thermal disorder effects. EXAFS data were analyzed and fitted using the WINXAS and IFEFFIT software packages. Theoretical scattering paths were calculated with FEFF8.2, including multiple scattering paths.

Figure 1 shows FT spectra of Se^{IV} sorbed on AFm-CO₃ equilibrated for 30 days. Suspensions with two different S:L ratios were used to prepare the pastes. Both samples had a Se^{IV} loading of 1000 ppm but for the sample with the lower S:L ratio a lower [Se]_{eq} was sufficient to obtain this loading. Comparison of the FT spectra of both Se^{IV} loaded AFm samples with the FT spectrum of a CaSeO₃ reference sample clearly shows the presence of a CaSeO₃ precipitate in the sample with the highest [Se]_{eq} whereas in the sample with the lower [Se]_{eq} only the oxygen shell of the SeO₃²⁻ anion could be detected suggesting that Se^{IV} sorbs through the formation of an outer sphere complex. In the case of Se^{IV} sorbed onto AFm-OHCO₃, the lower S:L ratio didn't have an impact of coordination environment of the sorbed Se^{IV} (data not shown). At both S:L ratios Se^{IV} sorbs on AFm-OHCO₃ through the formation of an outer sphere complex.

Figure 2 shows the XANES spectra of controlled oxidation experiments of Se^{II} sorbed onto AFm-CO₃. The XANES spectrum of the 3000 ppm sample shows a shoulder at the white line position of Se⁰, which grows into a distinct Se⁰ white line with decreasing Se concentration (1000 ppm and 500 ppm samples). This tendency is much less expressed by the corresponding AFm-OHCO₃ series as is evident from the XANES spectra in Figure 2b. Analysis of EXAFS spectra of pure Se^{II} loaded AFm-CO₃ and AFm-OHCO₃ samples measured in a previous campaign led to the conclusion that HSe⁻ sorbs prevalently in the interlayer space of AFm-OHCO₃, while sorption onto AFm-CO₃ occurs mainly on surface sites because of restricted access to the interlayer space. Since HSe⁻ in the interlayer space is better protected from oxidation than HSe⁻ at the outer surfaces, the present observations support this structural interpretation of EXAFS spectra

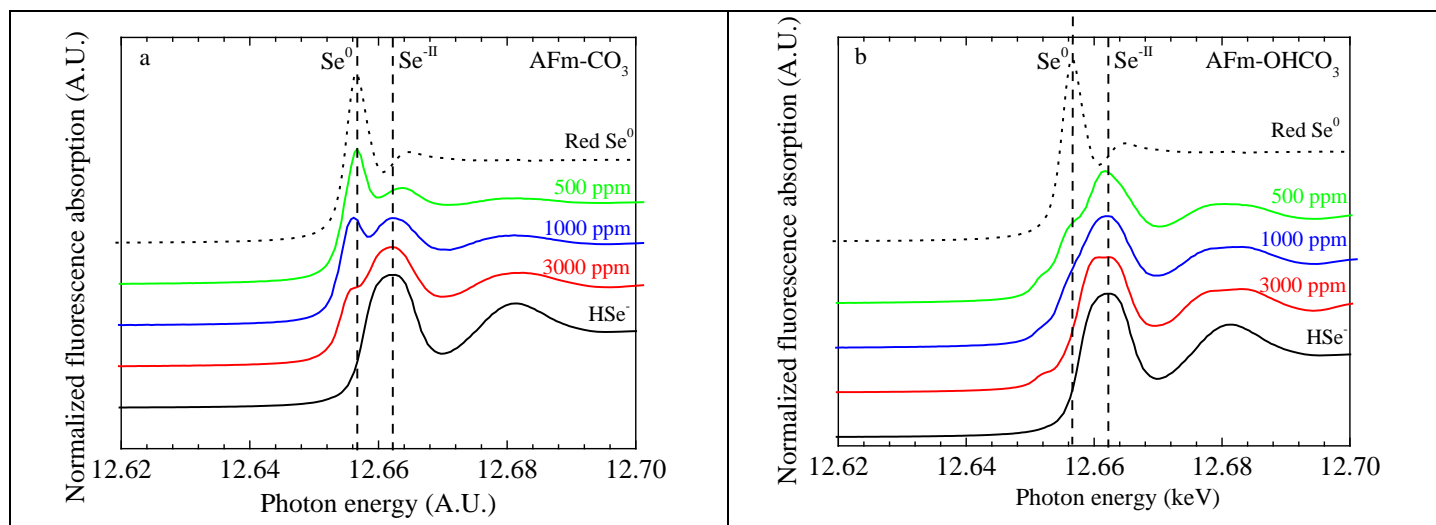


Fig. 2. XANES spectra of Se^{II} sorbed onto AFm-CO₃ (a) and AFm-OHCO₃ (b) at three different Se^{II} loadings as well as XANES spectra of Se⁰ and HSe⁻.

Conferences contributions:

- “Redox transformations and the disposal of radioactive waste: Influence on Se immobilization” **Wieland E., Rojo H., Scheinost A.C., Tits J.** Goldschmidt 2015 conference, 16-21 August, 2015, Prague, Czech republic. Presentation.
- “Selenium Uptake by Cementitious Materials: Effect of the Redox State”, **Tits J., Rojo H., Scheinost A.C., Wieland E.** Migration 2015 conference, 13 – 18 September, 2015, Santa-Fe NM, USA. Poster