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|  ESRF | Experiment title: Se speciation in cement phases using XAFS | Experiment number: CH 01-01 221 |
| Beamline: BM1A | Date of experiment: from: 08.12.2000 to: 12.12.2000 | Date of report: 22-02-01 |
| Shifts: 12 | Local contact(s): Hermann Emerich | <i>Received at ESRF:</i> |
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| Report: The retardation of radionuclides through engineered cementitious barriers is a key process concerning the confinement of nuclear waste stored in future underground Swiss repositories. Thus, a mechanistic understanding of processes controlling the uptake of radionuclides in cement systems is of fundamental importance for predicting the mobility and long-term fate of radionuclides in a waste repository. Among the safety relevant radionuclides, the role of ⁷⁹ Se is non-negligible given its long half-time period (1.1x10 ⁶ years). In a hydrated highly alkaline (pH = 12-14) cementitious environment, the chemical forms of selenium are Se ^{VI} O ₄ ²⁻ and Se ^{IV} O ₃ ²⁻ anions. We have performed Se K -edge XAFS measurements in transmission mode (reference samples) and in fluorescence mode (sorption samples) to assess the oxidation state and the chemical environment of Se ^{VI} O ₄ ²⁻ and Se ^{IV} O ₃ ²⁻ sorbed onto Portland cement and constitutive phases (portlandite: Ca(OH) ₂ , calcium silicate hydrate: (CaO) _x (SiO ₂) _y (H ₂ O) _z and AFT: [Ca ₃ (Al,Fe)(OH) ₆ .12H ₂ O] ₂ .X ₃ .zH ₂ O) for 1 day up to 63 days. The position of the absorption edge was carefully examined to check for possible redox processes. In Figure 1 the edge positions is displayed for a set of the reference compounds and the CSH sorption samples. The Se ^{VI} and Se ^{IV} edge positions are well grouped and allow a clear distinction between these two formal oxidation states. | | |

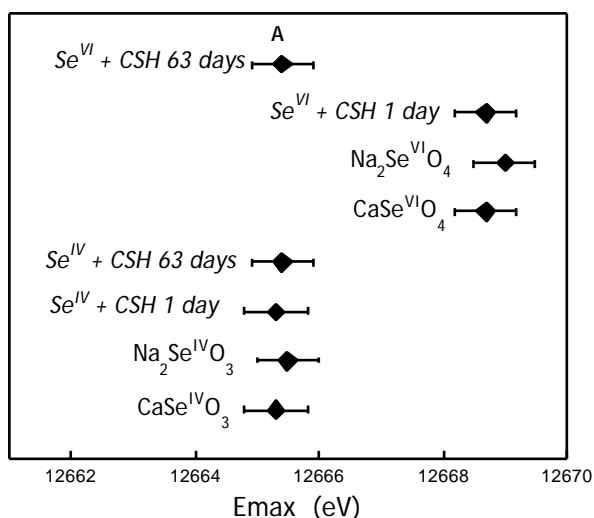


Figure 1: Absorption edge maximum energy of the Se K edge XANES spectra for references solution and CSH samples (italics).

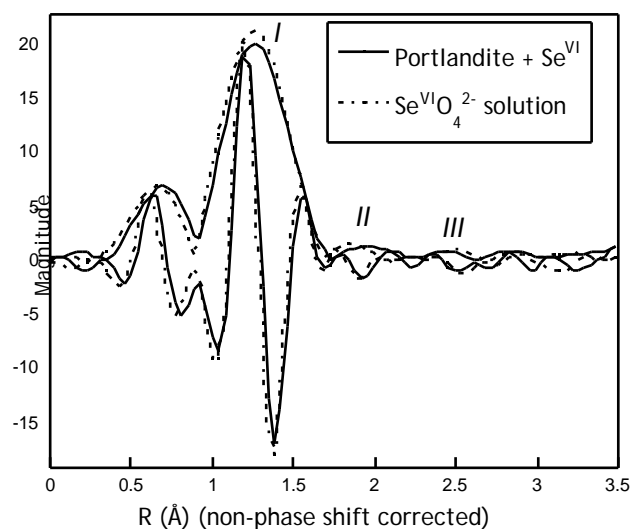


Figure 2: Pseudo-radial distribution of Se^{VI} in and sorbed on portlandite.

The figure reveals that the oxidation state remained unchanged upon selenium sorption except for $\text{Se}^{\text{VI}}\text{O}_4^{2-}$ sorbed on CSH for prolonged time (noted as A in Fig. 1). XANES deconvolution revealed that the samples consists of 80% Se^{VI} and 20% Se^{IV} . Complementary chemical experiments are now being undertaken to understand this reduction process.

Data analysis using Feff7.02 revealed that in most sorption samples Se is in a similar structural environment as in solution. This finding is illustrated in Fig. 2 showing the pseudo-radial distribution functions (PRDF's) of Se^{VI} sorbed on portlandite and a $\text{Se}^{\text{VI}}\text{O}_4^{2-}$ solution. Se-O distances (corresponding to peak I in Fig. 2) were found in the range of 1.69-1.70 Å for sorbed $\text{Se}^{\text{IV}}\text{O}_3^{2-}$ (1.70 Å for $\text{Se}^{\text{IV}}\text{O}_3^{2-}$ solution) and in the range 1.63-1.65 Å for sorbed $\text{Se}^{\text{VI}}\text{O}_4^{2-}$ (1.64 for $\text{Se}^{\text{VI}}\text{O}_4^{2-}$ solution), demonstrating that the rigid $\text{SeO}_{3/4}$ units are maintained upon sorption onto cement and cement constituents. The higher R features in the PRDF's (peak II and III in Fig. 2) could be simulated with multiple scattering paths inside the SeO_4 unit of the third and fourth order, respectively. The XAFS findings are hence in favour of an outer-sphere complexation model between the rigid SeO_4 unit and portlandite. Se^{VI} sorbed onto cement shows some deviation from this behaviour and a feature at $R+R = 1.9$ Å was observed which will further investigated through comparison with additional cement constitutive phases such as *AFm* ($\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-mono}$, $[\text{Ca}_2(\text{Al,Fe})(\text{OH})_6]\cdot X\cdot z\text{H}_2\text{O}$).