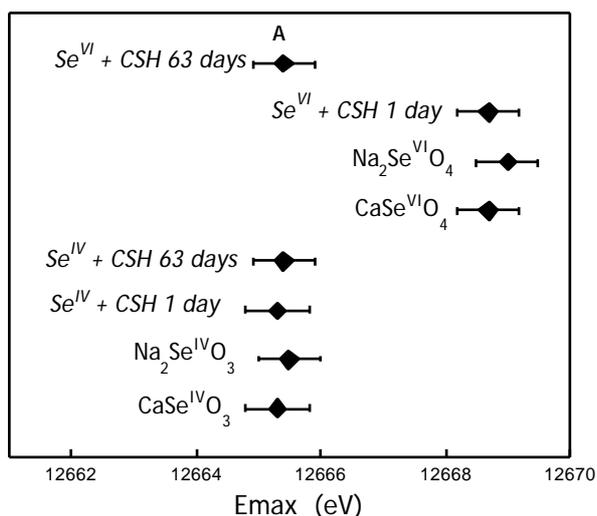
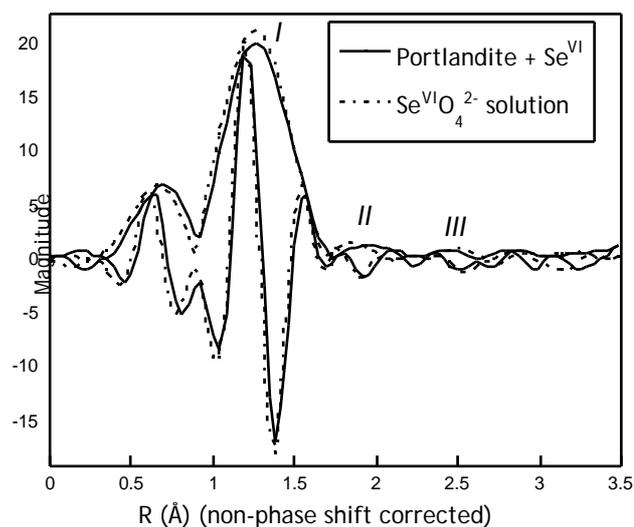




 ESRF	<b>Experiment title:</b> <b>Se speciation in cement phases using XAFS</b>	<b>Experiment number:</b> <b>CH 01-01 221</b>
<b>Beamline:</b> BM1A	<b>Date of experiment:</b> from: 08.12.2000 to: 12.12.2000	<b>Date of report:</b> 22-02-01
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<b>Names and affiliations of applicants</b> (* indicates experimentalists): I. Bonhoure , R. Dähn , Yan Tits , A. M. Scheidegger and E. Wieland. Waste Management Laboratory Paul Scherrer Institute, CH 5232 Villigen, Switzerland		
<b>Report:</b> 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 <sup>79</sup> Se is non-negligible given its long half-time period (1.1x10 <sup>6</sup> years). In a hydrated highly alkaline (pH = 12-14) cementitious environment, the chemical forms of selenium are Se <sup>VI</sup> O <sub>4</sub> <sup>2-</sup> and Se <sup>IV</sup> O <sub>3</sub> <sup>2-</sup> 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 <sup>VI</sup> O <sub>4</sub> <sup>2-</sup> and Se <sup>IV</sup> O <sub>3</sub> <sup>2-</sup> sorbed onto Portland cement and constitutive phases (portlandite: Ca(OH) <sub>2</sub> , calcium silicate hydrate: (CaO) <sub>x</sub> (SiO <sub>2</sub> ) <sub>y</sub> (H <sub>2</sub> O) <sub>z</sub> and AFT: [Ca <sub>3</sub> (Al,Fe)(OH) <sub>6</sub> .12H <sub>2</sub> O] <sub>2</sub> .X <sub>3</sub> .zH <sub>2</sub> 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 <sup>VI</sup> and Se <sup>IV</sup> 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  $\text{Se}^{\text{VI}}$  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%  $\text{Se}^{\text{VI}}$  and 20%  $\text{Se}^{\text{IV}}$ . 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  $\text{Se}^{\text{VI}}$  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  $\text{SeO}_4$  unit of the third and fourth order, respectively. The XAFS findings are hence in favour of an outer-sphere complexation model between the rigid  $\text{SeO}_4$  unit and portlandite.  $\text{Se}^{\text{VI}}$  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* ( $\text{Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-mono}$ ,  $[\text{Ca}_2(\text{Al,Fe})(\text{OH})_6]\cdot\text{X}\cdot\text{zH}_2\text{O}$ ).