



	Experiment title: Tin speciation in cement phases using XAS	Experiment number: ME-258
Beamline: BM1B	Date of experiment: from: 30-01-2002 to: 05-02-2002	Date of report: 26-08-2002
Shifts: 18	Local contact(s): Wouter Van Beek	<i>Received at ESRF:</i>
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The long half-life of ^{126}Sn ($t_{1/2} = 10^5$ y) implies that Sn could have a significant effect on cumulative radioactive dose if transported without retardation through the geosphere. Under the cement hydration condition, Sn is stable in its tetravalent form, Sn(IV) and Sn(OH)_5^- and Sn(OH)_6^{2-} are the dominating hydrolytic species. At the present time, no mechanistic studies on the uptake of Sn(IV) by HCP and CSH phases exist and it has been recently shown that the precipitation of CaSn(OH)_6 can occur if Sn(IV) is added to cement systems at concentrations higher than 10^{-6} M at $\text{pH} > 12.5$. Based on the Sn(IV) inventory in the cement system, we have then to consider two possible uptake processes: precipitation of CaSn(OH)_6 when supersaturation with respect to this solid is achieved and/or Sn(IV) sorption onto cement phases for undersaturation conditions. The goal of this XAS study ($\text{Sn K edge} = 29.2$ keV) was i) to directly prove the formation of $\text{Ca[Sn(OH)}_6]$ in cement systems, ii) to determine the local coordination environment of sorbed Sn(IV) in HCP in order to identify the Sn(IV) sorption mode (outer/inner-sphere surface complexation, incorporation, surface precipitation) iii) to identify the Sn(IV) uptake-controlling phase in HCP complex matrix. In HCP, for oversaturated conditions, the formation of CaSn(OH)_6 was clearly identified. Figure 1 displays the Sn pseudo-radial distribution functions (PRDFs, raw and calculated) for Sn immobilized (undersaturated conditions) on HCP and

CSH-0.7 (a, b). The first peak has been attributed to oxygen atoms ($6\text{O}@2.06\text{\AA}$). Two further peaks (respectively A and B) well above the noise level are clearly visible. These peaks are not present in $\text{CaSn}(\text{OH})_6$ PRDF so that the formation of this precipitate can be eliminated in these solids. Accordingly, data fitting revealed that Sn is immobilized as inner-sphere complexes: Sn(1) in HCP ($\text{Ca}@3.62\text{\AA}$; $\text{Si}/\text{Al}@4.10\text{\AA}$) and Sn(2) in CSH-0.7 ($\text{Ca}@3.62\text{\AA}$; $\text{Si}@4.10\text{\AA}$).

Tobermorite-1.1nm was used as structural model for CSH-0.7. Its structure consists of two Si tetrahedral layers connected to the CaO core with free Ca and H_2O molecules in the interlayer. Two possible Sn(2) structural models, implying a corner sharing between the Sn octahedra and Si tetrahedra, have been found.

The CSH based model could nevertheless not explain the inner-sphere complex formation in HCP (Sn(1)), indicating that CSH may not be the uptake-controlling phase for Sn(IV) in the cement matrix. An alternative structural model for Sn(1) can be proposed, assuming that ettringite is the uptake-controlling phase. Future XAS experiments are planned to verify this hypothesis.

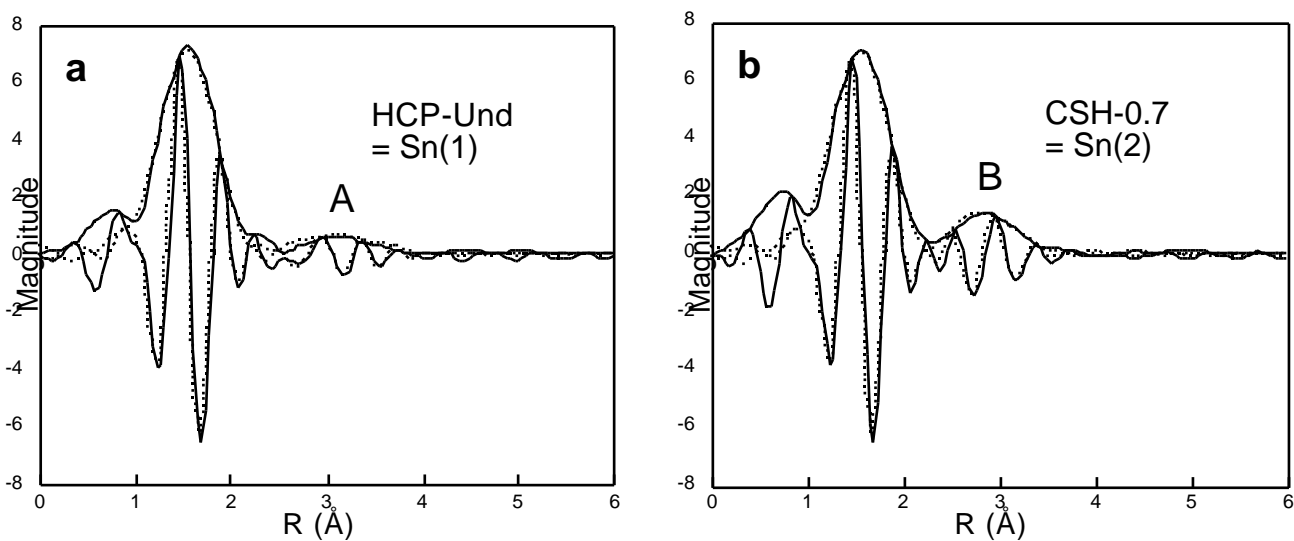


Figure 1. Sn K-edge raw (—) and simulated by FEFF (---) modulus and imaginary part of the PRDF for Sn(IV) immobilized in HCP (a) and CSH (b).