ESRF	**Experiment title:** **XAFS study on strontium uptake by cement**	**Experiment number**: **01-01-254**
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Report: In underground nuclear waste repositories, cementitious barriers are capable to significantly retard the migration of radionuclides into the host rock and, due to their long-term stability, cement phases control the long-term release of radionuclides. A detailed knowledge of the radionuclides/cement interaction is then crucial to predict the long-term fate of radionuclides and to quantify a possible release into the environment. The ^{90}Sr isotope belongs to the category of fission products found in operational waste from reactors and reprocessing plants. The study of this radionuclide interaction with cement is however complicated by the fact that the original cement matrix is also containing non-radioactive strontium. Consequently, the concentration and mobility of ^{90}Sr in the cementitious near-field is controlled by the interaction of ^{90}Sr with the stable ^{88}Sr of the cement matrix. To deepen our knowledge of this process, our goal was to determine the Sr speciation in original untreated cement and to quantify the interaction of the ^{90}Sr radionuclide with cement once it is leached by underground water and then the non-radioactive Sr removed. For this purpose, the concomitant use of batch experiments to monitor the cement depletion and loading with respect to Sr and of XAS to probe the local environment of Sr in cement was necessary. We have hence registered the Sr K edge at low temperature for strontium reference samples, including possible solubility limiting phases like strontianite ($SrCO_3$) and celestine ($SrSO_4$) and for different cement samples with various amount of Sr, obtained

by varying the number of depletion or loading steps. CSH (calcium silicate hydrates) samples contained sorbed or co-precipitated Sr were also taken into account as this solid phase is suspected to be responsible for most of the strontium uptake in hydrated cement. The results obtained with all the cement or CSH samples were comparable, at least for the first shell. As shown in Figure 1, the Sr PRDF in depleted cement do not correspond to those of $SrSO_4$ and $SrCO_3$ but is rather similar to the one of the strontium water solution. These two solid phases can hence be excluded as Sr containing phases in cement. The similarity between the strontium environment in solution and in cement has also been evidenced by fitting the first peak of the Fourier Transform using experimental phases and amplitudes extracted from SrO (cf. Table 1). The Sr-O distance do not differ significantly going from the solution (2.60 Å) to the cement or CSH (2.58-2.59 Å). The number of neighbors however decrease from 9.1 up to 6.5 implying a partial reduction of the hydration shell. For the untreated dry cement (containing original Sr) it has also been found two second Si neighbors at 3.54 Å. It can be deduced that the original Sr in cement is forming inner-sphere complexes with a Si-containing phase. The incorporation of Sr in the CSH structure by replacement of Ca is doubtful because it would imply much shorter distances (d Ca-O 2.35 Å in CSH). After the original Sr has been depleted, the Sr uptake by cement results in partially hydrated Sr ions, the reduction of water molecules being probably due to the interaction of Sr with the CSH phases.
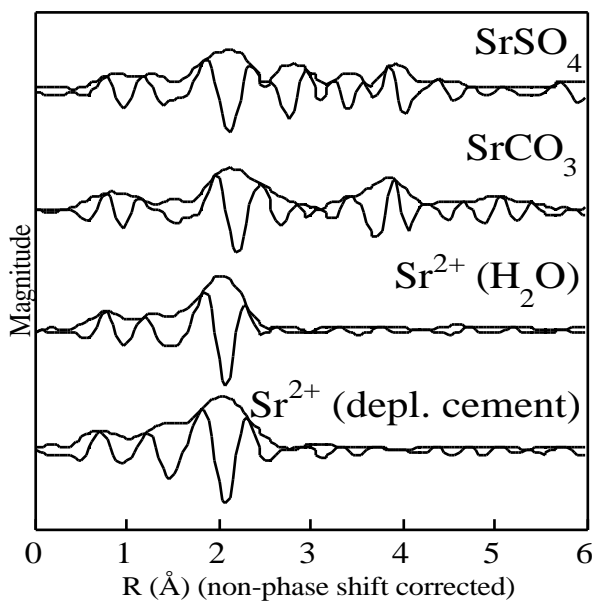

Samples	Fit results (Sr-O)				
	N	(Å)	R (Å)	E (eV)	rf (%)
Sr^{2+} (H_2O)	9.1	0.11	2.60	0	3.9
Sr^{2+} (depleted cement)	7.2	0.10	2.59	0	0.7
Sr^{2+} (untreated cement)	6.5	0.09	2.58	0	0.1
Sr^{2+} (CSH)	7.8	0.09	2.59	0	2.0

Figure 1: Modulus and imaginary part of the PRDF of the Sr K edge EXAFS oscillations.

Table 1: Best fit parameters for the first peak of the Sr PRDF using experimental functions.