



	<b>Experiment title:</b> EXAFS investigation of Pu(III) after uptake by crushed cement (HCP)	<b>Experiment number:</b> EV-262
<b>Beamline:</b> BM20	<b>Date of experiment:</b> from: 30.08.2017 to: 01.09.2017	<b>Date of report:</b> 10.09.2023
<b>Shifts:</b> 12	<b>Local contact(s):</b> André Rossberg	<i>Received at ESRF:</i> 12.09.2023
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### Report:

Five samples had been prepared and shipped to ESRF for this experimental run. During the entire beam time, the beam intensity showed such strong instabilities that only a few scans for three samples (Table 1) could be analysed. The liquid-nitrogen cooling system for the first Si(111) crystal (0°) of the new double-crystal monochromator, which had just been installed by FMB Oxford, was not functioning properly. During the beam time, technical support from FMB Oxford had to be called.

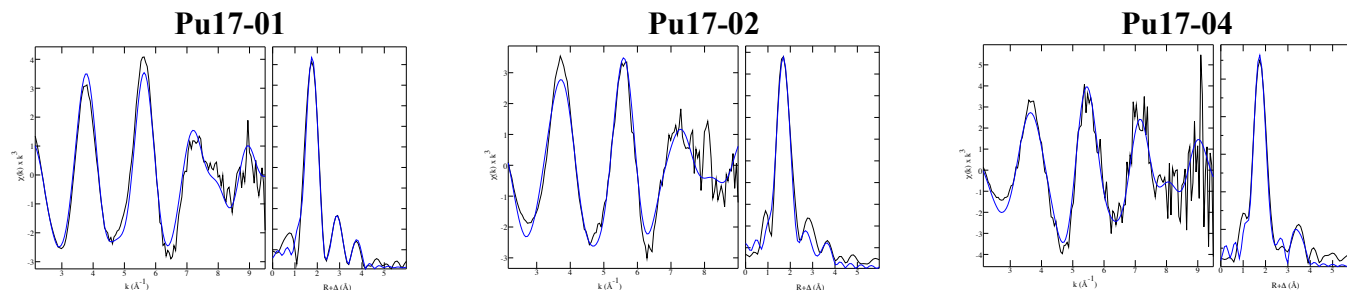
**Table 1** Chemical conditions of samples with Pu sorbed on hardened cement paste (HCP, water/cement = 0.5) in different electrolytes. All samples were prepared under Ar atmosphere with a solid-to-liquid ratio (S/L) of 2.5 g/L. The initial concentration was 5  $\mu\text{M}$   $^{239}\text{Pu(III)}$ . After three days for preconditioning, the contact time with Pu was three days. Phase separation was achieved by centrifugation with 108,000 g for 1 h. Electrolytes: VGL – German acronym for *Verdünnte Gipschlösung*,  $I = 2.5 \text{ M}$ , 2.523 M NaCl, 0.01 M  $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$ , 0.008 M  $\text{Na}_2\text{SO}_4$ , 0.0051 M KCl); VGL-ACW – artificial cement water obtained by leaching of HCP (S/L = 10 g/L) in VGL for seven days.

Sample ID	Electrolyte	Final pH	$E_h$ (SHE) mV	Pu loading ppm
Pu17-01	VGL	10.2	+20	553
Pu17-02	VGL-ACW	10.2	+100	632
Pu17-04	VGL-ACW	12.9	-140	169

Multiple scans of Pu  $L_3$ -edge (18057.0 eV) XAFS spectra were collected at 15 K in fluorescence mode using the 13-element Ge detector. For energy calibration, the Zr K-edge (17998.0 eV) XANES spectrum of a Zr

metal foil was measured simultaneously in transmission mode during each scan. The EXAFS data analysis was done with the software packages EXAFSPAK and FEFF9 using a structural model based on 14 Å tobermorite, where Ca in the CaO interlayer was replaced by Pu. The best model to the experimental data and the obtained structural parameters are shown in Figure 1 and Table 2, respectively.

**Figure 1** Raw  $k^3$ -weighted Pu L<sub>3</sub>-edge EXAFS spectra and best fit to the experimental data (left panel) together with the corresponding Fourier transform magnitudes (right panel). Black solid line – experiment, blue solid line – fit.



**Table 2** EXAFS structural parameters with  $N$  – coordination number,  $R$  – distance in Å. The energy shift,  $\Delta E_0$ , and the Debye-Waller factor,  $\sigma^2$ , of the O, Si, and Ca shells were fixed to the same value, respectively, and varied as global parameters.  $S_0^2$  was fixed to 0.9. Typical uncertainties are  $\pm 0.5$  atoms for  $N$ ,  $\pm 0.02$  Å for  $R$  and  $\pm 0.001$  Å<sup>2</sup> for  $\sigma^2$ , respectively.

Sample ID	Pu-O		Pu-Si		Pu-Si		Pu-Ca		$\sigma^2$ Å <sup>2</sup>	$\Delta E_0$ eV	Norm. error
	$N$	$R$	$N$	$R$	$N$	$R$	$N$	$R$			
Pu17-01	6.9	2.26	1.5	3.07	3.6	3.60	3.6	4.13	0.0132	3.0	0.191
Pu17-02	7.9	2.24	3.2	3.09			3.3	4.02	0.0161	-0.6	0.241
Pu17-04	7.0	2.26	2.0	3.03			3.9	4.05	0.0107	-0.9	0.968

The following conclusions can be drawn from these measurements:

- The energy of the Pu L<sub>3</sub>-edge XANES (not shown) and the average Pu-O distance of 2.24 – 2.26 Å are indicative for Pu(IV). This means that the initially added Pu(III) has been oxidized to Pu(IV) during the reaction in the HCP suspension.
- The EXAFS analysis did not show any evidence of Pu-Pu interaction, i.e., no polynuclear Pu species or precipitates could be observed.
- The detection of Si and Ca coordination shells of Pu allow to conclude that Pu (IV) has been taken up by calcium-silicate-hydrate (CSH) phases, the main constituent (50 wt.%) of HCP.
- The samples 02 and 04 prepared in VGL-ACW did not show a second Si shell at 3.60 Å as observed for sample 01 prepared in VGL. However, this difference could also be the result of uncertainties and noise in the EXAFS spectra and should be remeasured.
- In summary, the three samples show similar structural parameters indicative of Pu(IV) uptake by CSH phases of hardened cement. This agrees with results obtained at lower ionic strength, e.g., the EXAFS study of Gaona et al. (Environ. Sci. Technol. 2011, 45, 8765-8771) on the uptake of Np(IV) by CSH phases and cement paste.