

	Experiment title: EXAFS investigation of Pu(III) after uptake by crushed cement (HCP)	Experiment number: EV-262
Beamline: BM20	Date of experiment: from: 24.02.2018 to: 28.02.2018	Date of report: 10.09.2023
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Report:

During this experimental run, ten samples could be measured by Pu L₃-edge EXAFS spectroscopy at 15 K in fluorescence mode. The Si(111) DCM was equipped with the 30° crystal set. Unfortunately, this resulted in 15 eV wide glitch in the energy range from 18284.6 eV to 18299.9 eV. Therefore, the k -range from 7.72 to 7.98 Å⁻¹ (5 data points) was strongly affected. The normalization of the fluorescence signal by I_0 could not normalise out this glitch (see Figure 1).

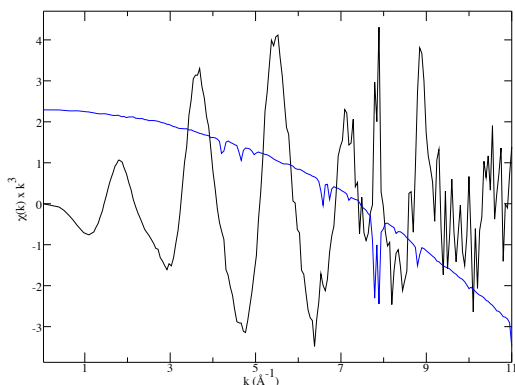


Figure 1 Raw k^3 -weighted Pu L₃-edge EXAFS spectrum (black line) and corresponding I_0 signal (blue line). The glitch at ≈ 7.8 Å⁻¹ is caused by the pair of Si(111) crystals with 30° crystal orientation. The Si(111) crystals with 0° orientation did not show this glitch (s. Exp. Report EV-262 for 2017).

The analysis showed that most of the EXAFS structural parameters obtained before and after deglitching were identical. A few exceptions occurred for the Pu-Ca shell at $R > 4$ Å due to the strong

correlation between coordination number and corresponding Debye-Waller factor. Despite this glitch, it was possible to analyse the EXAFS data in the k -range from 2.1 – 9.5 Å⁻¹. The results have been included in three manuscripts (see below).

Publications based on this experimental run:



Article

Uptake of Actinides by Hardened Cement Paste in High-Salinity Pore Water

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Abstract: The interaction of the actinides Pu(III) as well as Am(III), Np(V), Np(VI) and U(VI) with hardened cement paste (HCP), prepared from ordinary Portland cement, was investigated by batch experiments in diluted caprock solution ($I = 2.5$ M) as a function of solid-to-liquid (S/L) ratio (0.5–20.0 g L⁻¹) and pH (9–13). Independent of the oxidation state of the actinides, strong sorption was observed with R_d values between 10³ – 10⁷ L kg⁻¹. For the hexavalent actinides U(VI) and Np(VI), a decrease in sorption was observed with increasing pH values, which could be due to the formation of the AnO₂(OH)₄²⁻ species. CE-ICP-MS measurements of the supernatant solution from the U(VI) batch sorption experiment at pH > 9 show that UO₂(OH)₃⁻ and UO₂(OH)₄²⁻ dominate the speciation. Pu L_{III}-edge XANES and EXAFS measurements showed oxidation of Pu(III) to Pu(IV) when interacting with HCP. Calcium-silicate-hydrate (C-S-H) phases effectively immobilize Pu(IV) by incorporating it into the CaO layer. This was observed in a C-S-H sample with C/S = 1.8 and HCP at pH 12.7. A comparison with data published in the literature on the retention of actinides on cement at low ionic strength showed that the influence of high ionic strength ($I = 2.5$) on the sorption behaviour was insignificant.

Keywords: sorption; speciation; actinides; cement; high ionic strength; XANES; EXAFS; CE-ICP-MS

This submission has been reviewed and requires major revision.

Uptake of Pu(IV) by hardened cement paste in the presence of gluconate at high and low ionic strengths

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Keywords: Sorption, ionic strength, plutonium, ordinary Portland cement, gluconate, EXAFS, XANES

Abstract

The uptake of Pu(IV) by hardened cement paste (HCP) at degradation stage I was investigated in the absence and presence of gluconate (GLU). Furthermore, the influence of the ionic strength was examined by different background electrolytes. For low ionic strength ($I = 0.3$ M) artificial cement pore water (ACW, pH = 13) and for high ionic strength ($I = 2.5$ M) cement pore water based on the diluted caprock solution (ACW-VGL, pH = 12.5) were used. Sorption experiments were performed under Ar atmosphere using HCP in the binary system HCP / GLU ($[GLU]_0 = 1 \times 10^{-1} - 1 \times 10^{-8}$ M) and the ternary system HCP / Pu(IV) / GLU ($[^{239}\text{Pu(IV)}]_0 = 1 \times 10^{-8}$ M, $[GLU]_0 = 1 \times 10^{-2}$ M) with solid-to-liquid ratios (S/L) of 0.1 – 50 g L⁻¹ within a contact time of 72 h. GLU sorbs strongly on HCP; a saturation of the sorption sites of HCP with GLU was observed at $[GLU] \geq 1 \times 10^{-4}$ M at S/L = 5 g L⁻¹. The effects of the order of addition of the components Pu(IV) and GLU showed a low sorption of Pu(IV) to HCP. In the absence of GLU, quantitative uptake ($S\% = 99\%$) of Pu(IV) by HCP was observed. GLU had a significant effect on the sorption of Pu(IV) to HCP independent of the ionic strength of both background electrolytes.

For XAFS measurements powder samples with Pu ($[Pu(\text{III})]_0 = 5 \times 10^{-6}$ M) sorbed on HCP (S/L = 2.5 g L⁻¹) were prepared in ACW and ACW-VGL, respectively, at pH \approx 13. With ACW-VGL as electrolyte, one additional sample was prepared in the presence of GLU ($[GLU]_0 = 1 \times 10^{-2}$ M) for comparison. Pu L_{III}-edge XANES spectra indicated that after uptake by HCP Pu is in the tetravalent oxidation state. The EXAFS structural parameters and comparison with literature indicate incorporation of Pu(IV) into calcium-silicate-hydrates phases of HCP. The different ionic strengths and the presence of GLU had no influence on the near-neighbor environment of Pu in HCP.

This submission has been reviewed and requires minor revision.



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Influence of gluconate on the retention of Eu(III), Am(III), Th(IV), Pu(IV), and U(VI) by C-S-H (C/S = 0.8)

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The retention of actinides in different oxidation states (An(X), X = III, IV, VI) by a calcium-silicate-hydrate (C-S-H) phase with a Ca/Si (C/S) ratio of 0.8 was investigated in the presence of gluconate (GLU). The actinides considered were Am(III), Th(IV), Pu(IV), and U(VI). Eu(III) was investigated as chemical analogue for Am(III) and Cm(III). In addition to the ternary systems An(X)/GLU/C-S-H, also binary systems An(X)/C-S-H, GLU/C-S-H, and An(X)/GLU were studied. Complementary analytical techniques were applied to address the different specific aspects of the binary and ternary systems. Time-resolved laser-induced luminescence spectroscopy (TRLFS) was applied in combination with parallel factor analysis (PARAFAC) to identify retained species and to monitor species-selective sorption kinetics. ¹³C and ²⁹Si magic-angle-spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy and X-ray photoelectron spectroscopy (XPS) were applied to determine the bulk structure and the composition of the C-S-H surface, respectively, in the absence and presence of GLU. The interaction of Th(IV) with GLU in different electrolytes was studied by capillary electrophoresis-inductively coupled plasma mass spectrometry (CE-ICP-MS). The influence of GLU on An(X) retention was investigated for a large concentration range up to 10⁻² M. The results showed that GLU had little to no effect on the overall An(X) retention by C-S-H with C/S of 0.8, regardless of the oxidation state of the actinides. For Eu(III), the TRLFS investigations additionally implied the formation of a Eu(III)-bearing precipitate with dissolved constituents of the C-S-H phase, which becomes structurally altered by the presence of GLU. For U(VI) sorption on the C-S-H phase, only a small influence of GLU could be established in the luminescence spectroscopic investigations, and no precipitation of U(VI)-containing secondary phases could be identified.

KEYWORDS

actinide, organic ligand, sorption, cementitious material, concrete, luminescence