

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

Janina Stietz *, Samer Amayri, Verena Häußler, Raphael Scholze and Tobias Reich *

Department of Chemistry, Johannes Gutenberg-Universität Mainz, 55099 Mainz, Germany; amayri@uni-mainz.de (S.A.)

* Correspondence: jastietz@uni-mainz.de (J.S.); treich@uni-mainz.de (T.R.); Tel.: +49-6131-39-36184 (J.S.); +49-6131-39-25250 (T.R.)

1. Supplementary Information

1.1. S1 XRF Measurements of OPC and HCP

Ordinary Portland cement (OPC) (PZ Doppel N CEM 1 42.5 N, Dyckerhoff, Germany) and hardened cement paste (HCP) ($w/c = 0.5$) were characterized using X-ray fluorescence (XRF) measurements with the routine programme using the standard calibration. The MagiXPRO XRF spectrometer (Philips, The Netherlands) was used for the sample with OPC and the Axios XRF spectrometer (Panalytical, United Kingdom) was used for the HCP sample. To determine the main elements, a melting tablet was used as an annealed sample. For the trace elements, a powder compact was prepared. Rh was utilized as the anode with an excitation power of 3.6 kW. The qualitative and quantitative determination of the elemental composition can be found in Table S1 and Table S2, respectively. The error in the determination with XRF is approximately 3%.

Table S1. Results of the XRF measurements for the main components of OPC and HCP in w%.

	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	SO ₃	MgO	K ₂ O	TiO ₂	Na ₂ O	P ₂ O ₅	MnO	LOI
OPC	65.4	22.3	3.6	2.8	2.6	1.4	0.8	0.2	0.2	0.2	0.03	2.7
HCP	66.0	22.4	3.6	2.8	2.1	1.3	0.1	0.2	0.1	0.1	0.03	26.8

Table S2. Results of the XRF measurements for the trace elements of OPC and HCP in ppm.

	Co	Cr	Cu	Nb	Ni	Pb	Rb	Sr	Th	U	V	W	Y	Zn	Zr
OPC	8.0	55.5	85.5	4.0	24.5	2.0	13.5	1182.5	2.8	3.3	28.0	30.5	8.5	363.5	68
HCP	8.0	45.2	66.3	2.4	16.6	2.5	2.1	833.4	2.0	0.0	29.9	1.9	7.0	277.7	51.0

1.2. S2 Powder XRD of HCP

The X-ray diffraction (XRD) measurements of the HCP powder ($w/c = 0.5$ and fraction $<63 \mu\text{m}$) were used to study the structure, composition, and physical properties of the materials. The measurements were performed on 10 mm of the irradiated sample surface. For these experiments a Seifert XRD3000 TT diffractometer (Eigenmann GmbH, Germany) with an automatic divergence slit (ADS) using Cu K α radiation and a secondary monochromator was used. A step width of $0.03^\circ 2\theta$ and a step counting time of 2 s were chosen. For the evaluation of the powder diffractogram the software Match! (Version 3.4.1, Crystal Impact, Germany) was used in combination with the COD (Crystallography Open Database, COD-Inorg REV189751 2017.01.03). By evaluating the diffractogram of the HCP sample, the most important phases of cement could be assigned, such as portlandite (COD ID: 7020139), alite (COD ID: 9014363), calcite (COD ID: 7022028) and ettringite (COD ID: 9011577). These are identified in Figure S1. Portlandite, calcite and ettringite belong to the main constituents of the hydrated hardened cement paste, while alite is a clinker phase of the cement. However, the most intensive signals of the diffractogram are all attributable to portlandite. Some of the signals show many small reflexes that stand out from the background, which could be identified as tobermorite. In these areas, the corresponding

intensities cannot be attributed exclusively to the phases identified but may indicate the presence of C-S-H phases in the sample, which are another main component of the hydrated hardened cement paste.

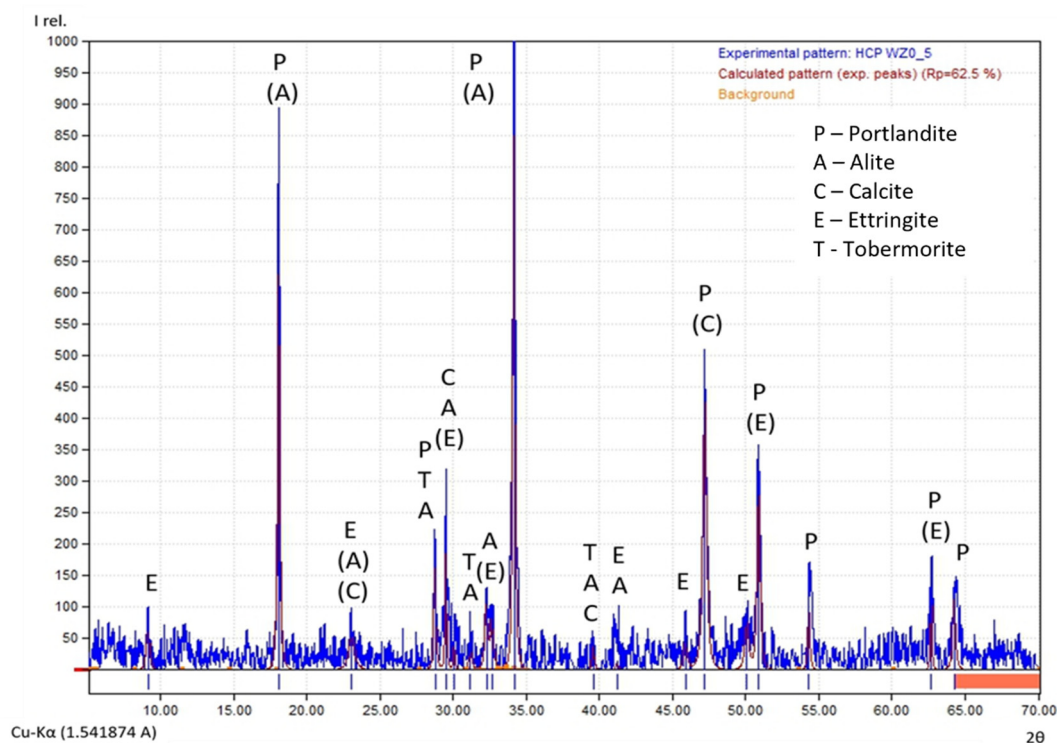


Figure S1. XRD pattern of the HCP sample with $w/c = 0.5$ (size fraction $<63 \mu\text{m}$) and assignment of the reflections to portlandite, alite, calcite and ettringite. The tobermorite could show the theoretical position of the most significant reflexes of C-S-H phases.

1.3. S3 XPS Analysis of HCP

The crushed and dried HCP powder ($w/c = 0.5$ and fraction $<63 \mu\text{m}$) were further analyzed by X-ray photoelectron spectroscopy (XPS) to determine the solids' surface composition. The measurements were performed with an XPS spectrometer from SPECS Surface Nano Analysis GmbH, Germany using an X-ray tube with an Al-Mg double anode and a PHOIBOS 100 MCD energy analyzer (SPECS Surface Nano Analysis GmbH, Germany). The measurement was recorded using SpecsLab measurement software (SPECS Surface Nano Analysis GmbH, Berlin, Germany). The analysis was performed using CasaXPS version 2.3.24PR1.0 (Casa Software Ltd, Teignmouth, United Kingdom). Calcium silicate powder (CaSiO_3 , Sigma-Aldrich, USA) with a known atomic ratio of calcium to silicon was used as reference sample to determine the corresponding XPS sensitivity factor $S_{\text{Si/Ca}}$. Figure S2 shows the XPS spectra of HCP samples ($S/L = 5 \text{ g L}^{-1}$) before and after contact with the background electrolyte VGL (German acronym for *Verdünnte Gipschlösung*, diluted caprock solution) at pH 12.8 for 72 h. After contact with VGL, the XPS lines of Na and Cl could be observed. The relative intensities of the Ca 2p and Si 2p XPS lines indicate that the Ca/Si ratio of the HCP surface becomes significantly smaller after contact with VGL (see Table S3). The atomic Ca/Si ratios were determined using equation S1, with $S_{\text{Si/Ca}} = 0.22$.

$$\frac{n_{\text{Ca}}}{n_{\text{Si}}} = \frac{I_{\text{Ca 2p}}}{I_{\text{Si 2p}}} \cdot S_{\text{Si/Ca}} \quad (\text{S1})$$

Table S3. Atomic Ca/Si ratios of HCP before and after contact with VGL determined by XPS (the estimated uncertainty is about $\pm 10\%$). (* = Reference sample)

Solid phase	Ca/Si-Ratio
CaSiO ₃ reference	1*
HCP (w/c 0.5)	3.45
HCP / VGL (w/c 0.5)	2.58

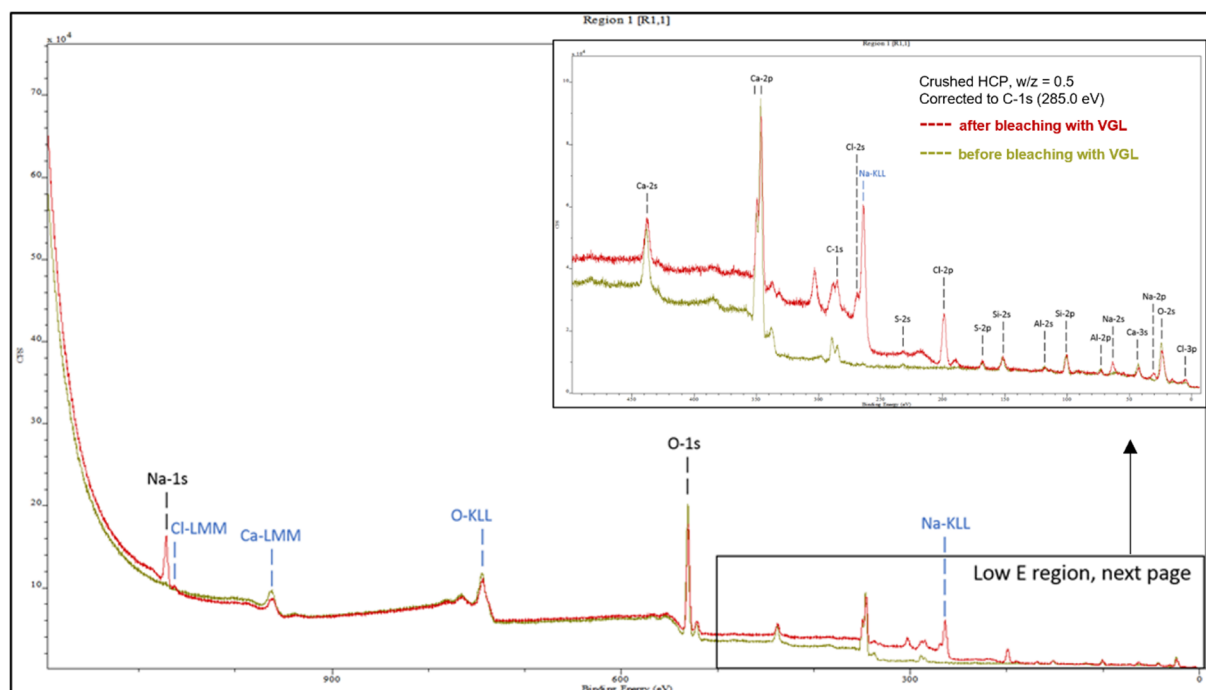


Figure S2. Result of the XPS measurements of HCP powder (w/c 0.5) before and after contact with VGL at pH 12.8 for 72 h. Ca-LMM and O-KLL denote Auger transitions. The other signals were assigned to the XPS lines of the contained elements.

1.4. S4 N₂-BET Measurement of HCP

The specific surface area of the HCP powder (w/c of 0.5; fraction < 63 μm) was determined by N₂ sorption according to the method of Brunauer, Emmett and Teller (BET) [1]. For the determination of the specific surface area a N₂-BET three-point analysis was established with a NOVA 1200 system (Quantachrome instruments, USA). The HCP powder was dried at 60 °C for 20 h. α -alumina (CRM 171, Sigma-Aldrich, USA) powder with a specific surface area of $S = 2.95 \text{ m}^2/\text{g}$ was used as reference. The determined specific surface area of the HCP powder agrees well with the literature data of Odler et al. [2] (see Table S4).

Table S4. N₂-BET specific surface areas of the HCP powder (w/c = 0.5 and size fraction <63 μm).

Samples	S(average) m ² g ⁻¹
HCP	9.91 \pm 0.66
HCP [2]	9.5

1.5. S5 CEC of HCP

To obtain an estimate for the cation exchange capacity (CEC) of the HCP powder (w/c of 0.5; fraction < 63 μm), sorption experiments ($S/L = 67 \text{ g L}^{-1}$; $V = 40 \text{ mL}$) with Na⁺ in 0.3 M NaOH, using ²²Na⁺ (195 kBq; PerkinElmer, Germany) as radioactive tracer, similar to the literature [3], were performed. The tracer content in the supernatant after centrifugation was determined by γ -ray spectroscopy using the γ -line at 1274.5 keV. The results are

shown in Table S5. From the here determined CEC and the specific surface area S_{BET} determined by the N_2 BET measurements, the sorption site density S_d was calculated using equation S2 (N_A is Avogadro constant):

$$S_d = \frac{CEC \cdot N_A}{S_{BET}} \quad (S2)$$

Table S5. pH values, distribution coefficients R_d , percentage of sorption, CEC_{Na} with $^{22}Na^+$ and HCP (S/L = 67 g L⁻¹) in VGL and Milli-Q after 72 h contact time. The calculated site density for the surface areas are also listed.

Sample	pH _{start}	pH _{end}	R_d / L kg ⁻¹	Sorption / %	CEC_{Na} / mol L kg ⁻¹	Site density / sites/nm ⁻²
HCP Milli-Q	12.8	13.3	0.2	1.1	0.05	3
HCP VGL	12.7	13.2	0.2	1.1	0.05	3

1.6. S6 Pu L_{III}-edge XANES Spectra

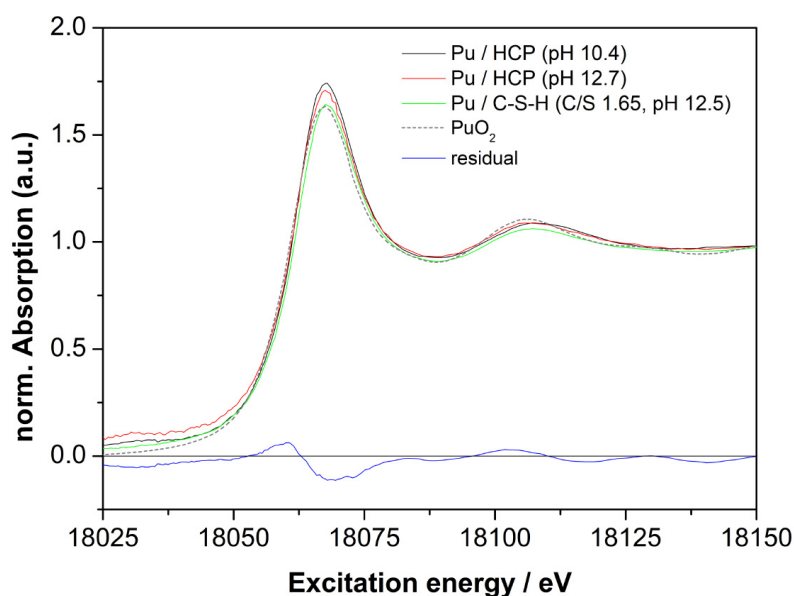


Figure S3. Normalized Pu L_{III}-edge XANES spectra of the samples HCP/Pu at pH 10.4 as well as at pH 12.7 and C-S-H-phase (C/S 1.65)/Pu at pH 12.5. The largest residual of all fits is shown as blue line. The raw data for the reference spectrum of PuO₂ were provided by P. Martin [4].

References

1. Wedler, G.; Freund, H.-J. *Lehrbuch der Physikalischen Chemie*; Wiley-VCH: Weinheim, Germany, 2012.
2. Odler, I. The BET-specific surface area of hydrated Portland cement and related materials. *Cem. Concr. Res.* **2003**, *33*, 2049–2056.
3. Hong, S.-Y.; Glasser, F.P. Alkali binding in cement pastes: Part I. The C-S-H phase. *Cem. Concr. Res.* **1999**, *29*, 1893–903.
4. Martin, P.; Grandjean, S.; Valot, C.; Carlot, G.; Ripert, M.; Blanc, P.; Hennig, C. XAS study of (U1-yPu)yO₂ solid solutions. *J. Alloys Compd.* **2007**, *444*, 410–414.