

IMPACT OF FORMATE, CITRATE AND GLUCONATE ON THE UPTAKE OF AN(III)/LN(III) AND AN(IV) BY CEMENT

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Abstract

In the context of low and intermediate level nuclear waste (L/ILW), cementitious materials are widely used for the conditioning and storage of the waste, as well as for the construction of engineered barrier systems (backfill, container and liner materials). The main solid phases in hydrated cements (calcium silicates hydrates (C-S-H), ettringite, monosulfoaluminate, monocarboaluminate, and hemicarboaluminate (AFm phases)) can retain radionuclides present in the waste, thus preventing or slowing down their release from the disposal site. Soluble small organic molecules are expected in the repository as a component of the emplaced waste, as degradation products of organic components disposed of, but also as additives in different cement formulations. The potential interaction of these organic ligands with actinides may importantly alter both their solubility and sorption properties. Although expected to be weak, the interaction of organic ligands with cement hydrates can also alter the surface properties of the latter. This study aims at a quantitative description of the interaction of low molecular weight organics (formate, citrate and gluconate) with selected cement phases, *i.e.* AFm, ettringite and C-S-H phases. The impact of these organic ligands on the uptake of Eu(III), Cm(III) and Pu(III/IV) by cement and individual cement phases is investigated with a combination of sorption experiments and advanced spectroscopic techniques.

The cement phases AFm, ettringite and C-S-H (with Ca/Si ratio C/S = 0.8-1.4) were prepared and stored under N₂ atmosphere with a solid to liquid ratio (S:L) of ≈ 50 g·dm⁻³, and equilibrated for 2 months before further use. Sorption experiments were performed with the synthesized cement phases in the presence of formate, citrate or gluconate at 10^{-4} M \leq [L] \leq 0.1 M and at pH \approx 13.3. The samples were filtered with 0.45 μ m nylon filters, and dried in a desiccator (37% relative humidity) for 14 days. The separated solid phases were characterized by X-ray diffraction (XRD), thermogravimetric analysis and FT-IR analysis. Supernatant solutions were characterized after filtration by ICP-OES (Ca, Al, Si, Na, sulfate) and NPOC (total organic content). Sorption experiments with ¹⁵²Eu + ^{nat}Eu and ²⁴²Pu were carried out in the absence

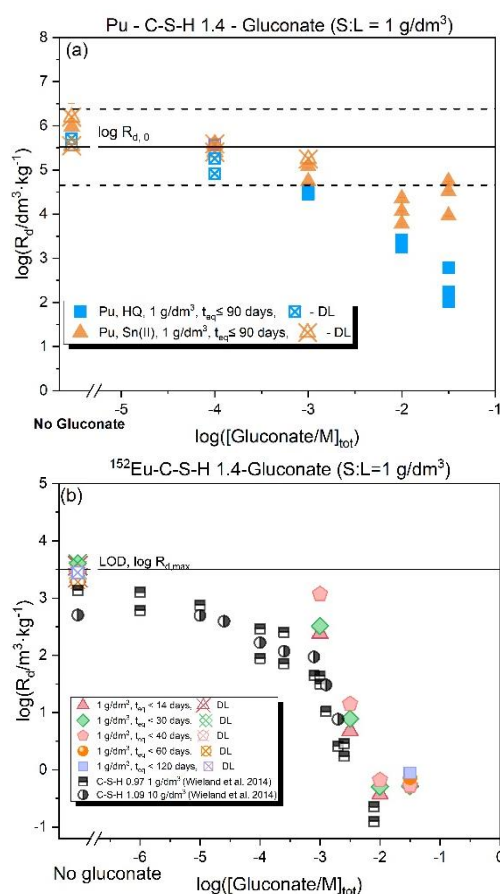


Figure 1. R_d values determined for the uptake of (a) Pu(III/IV) and (b) Eu(III) by C-S-H 1.4 in the absence and presence of GLU at pH=13.3. Solid line indicates the $R_{d,0}$ values in the absence of gluconate. Symbols crossed with X correspond to samples at /below the detection limit (DL).

and presence of organic ligands and varying the S:L ratio, order of addition and organic concentration. In the sorption experiments with plutonium, redox conditions were buffered with hydroquinone (HQ, $\text{pe} + \text{pH} \approx 9$) or Sn(II)Cl_2 ($\text{pe} + \text{pH} \approx 1.5$). Phase separation was achieved by ultrafiltration via 10 kD filters. The measurement of ^{242}Pu and ^{152}Eu was carried out by ICP-MS and gamma counter analysis respectively. TRLFS investigation was conducted exclusively on the Cm(III)-C-S-H-GLU system. Both solution and solid phase speciation were investigated at the same pH and ligand concentrations considered in the sorption experiments. TRLFS spectra were collected for equilibration times $7 \leq t_{\text{eq}}$ (days) ≤ 56 .

Formate sorption was found to be very weak ($R_d \approx 10^{-3} \text{ m}^3 \cdot \text{kg}^{-1}$) for all investigated cement phases (AFm, ettringite and C-S-H), in agreement with previous observations reported in the literature [1]. Significantly higher R_d values were quantified for the uptake of citrate and gluconate. The uptake of citrate and gluconate by C-S-H phases with $\text{Ca/Si} = 0.8\text{-}1.4$ was found to be relatively high with $R_d \approx 10^{-3} - 10^{-2} \text{ m}^3 \cdot \text{kg}^{-1}$. Furthermore, both gluconate and citrate show a systematic increase in $\log R_d$ values with increasing Ca/Si ratio. This observation hints towards a Ca complexation mediated process at the surface of C-S-H phases. This mechanism has been recently validated by molecular dynamics calculations for the C-S-H-gluconate system [2]. Formate and citrate have a negligible impact on the uptake of Pu(III/IV) by C-S-H phases for both redox-buffer systems. Figure 1 shows the $\log R_d$ values for the uptake of Pu (a) and Eu (b) by C-S-H phases with C/S ratios of 1.4 as a function of gluconate total concentrations ($10^{-4} \text{ M} \leq [\text{GLU}]_{\text{tot}} \leq 10^{-1.5} \text{ M}$). In line with previous studies with Th(IV) and Eu(III) [3], gluconate significantly decreases the uptake of Pu(III/IV) and Eu(III) by C-S-H phases. These observations are explained by the possible formation of stable ternary / quaternary complexes in the aqueous phase, *i.e.* Ca-An(IV)-OH-GLU and $\text{Ca-An(III)/Ln(III)-OH-GLU}$ [4, 5]. Figure 1(a) shows also that $\log R_d$ values determined at the two highest ligand concentrations in the Sn(II) -buffered system follow a rather increasing trend, opposite of that observed in the HQ-buffered system. This finding hints towards (i) a different chemical behavior induced by the redox buffer, expectedly involving the predominance of Pu(IV) and Pu(III) for HQ and Sn(II) systems, respectively, and (ii) the possibility of a co-adsorption process of $\text{Pu(III)}_{\text{aq}}$ with GLU and the subsequent surface complexation of Pu onto these GLU-complexed surface sites, as also observed in [6]. TRLFS confirmed the key role of Ca in the formation of quaternary aqueous complexes $\text{Ca-An(III)/Ln(III)-OH-GLU}$, whereas at low ligand concentrations the incorporation of Cm(III) in the C-S-H structure was observed. This experimental study was complemented with molecular dynamics calculations on the binary and ternary systems defined by C-S-H / Eu(III) / GLU, which provide key insights for the mechanistic understanding of the retention processes in cementitious systems [7].

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