Impact of formate, citrate and gluconate on the uptake of radionuclides by cement: study of the binary and ternary systems cement-L and cement-RN-L

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In the context of low and intermediate level nuclear wastes (L/ILW), cementitious materials are widely used for the conditioning and storage of the waste, as well as for the construction of the engineered barrier systems (backfill, container and liner materials). The main solid phases in the cementitious matrix (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 hard-Lewis acids such as actinides may importantly alter both solubility and sorption properties of these radionuclides. Although expectedly considered weak, the interaction of organic ligands with cement can also alter the surface properties of the latter and thus deserve close attention.
In this framework, 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 phases, ettringite and C-S-H. 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 also investigated with a combination of sorption experiments and advanced spectroscopic techniques (TRLFS and XAFS).

The cement phases AFm, ettringite and C-S-H (with Ca/Si ratio C:S = 0.8-1.4) were prepared and stored under N_2 atmosphere with a solid to liquid ratio (S:L) of ≈50 $g \cdot dm^{-3}$, and equilibrated for 2 months before further use. Sorption experiments were performed under constant agitation (end-over-end shaker) with the synthesized cement phases in the presence of formate, citrate or gluconate at 10^{-4} M ≤ [L] ≤ 0.1 M. Preliminary kinetic sorption experiments were performed at t = 1 – 14 days, whereas sorption isotherms were collected at t = 7 days. The samples were filtered with 0.45 μm 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 ^{152}Eu + ^{nat}Eu and ^{242}Pu were carried out in the absence 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 (pe + pH ≈ 9) or $Sn(II)Cl_2$ (pe + pH ≈ 1.5).

Measurements of the organic concentrations show that the sorption of formate on AFm phases and ettringite is very weak, consistently with previous observations reported in the literature [1]. A significant uptake is observed for citrate on monosulfoaluminate (Ms), monocarboaluminate (Mc) and hemicarboaluminate (Hc), with average R_d values of ≈ 0.2, ≈ 0.1 and ≈ 0.3 $m^3 \cdot kg^{-1}$, respectively. Similar R_d values are quantified for the uptake of citrate and gluconate by ettringite, with R_d ≈ 0.1 $m^3 \cdot kg^{-1}$. Changes in the chemical structure of the cement phases due to the intercalation of the organic anions are visible only at high organic concentrations. Results of the kinetic and sorption experiments with C-S-H phases (C:S = 0.8-1.4) indicate the organics uptake occurs trough Ca-organics complexes formation and the uptake rate increases with the increase of Ca:Si ratio. Results of the on-going sorption experiments with Pu and Eu in presence and absence of organic ligands will be thoroughly discussed in this contribution.

[1] Wieland, E., Jakob, A., Tits, J., Lothenbach, B., Kunz, D. (2016). Applied Geochemistry, 67, 101-117

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