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Sorption of isosaccharinic acid (ISA) by hydrated cement paste and C-S-H phases

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1. Introduction

Geological repository systems for radioactive waste disposal are designed to prevent or minimize the release of radionuclides (RN) into the biosphere. In the case of low- and intermediate-level radioactive waste (LILW) repository systems, cementitious materials such as concrete, mortar, and grout are widely used as structural components, waste forms, and chemical/physical stabilizers. Due to their high sorption capacity for both cations and anions, cement paste is expected to strongly retain RN in LILW repository systems. Cementitious pore solution is characterized by high pH values (10–13.5) and elevated concentrations of K, Na and Ca. These boundary conditions define the retention properties of RN in LILW repositories.

Cellulosic materials such as papers, wipes, cottons, woods, and filter materials are expected in large inventories in LILW. They are not stable in the hyperalkaline conditions defined by cement, and degrade into soluble organic materials with smaller molecular weight, such as isosaccharinic acid ($C_6H_{12}O_6$, ISA). ISA has been reported to form strong and stable complexes as a hard Lewis base with metal ions such as Th, U, Np, Pu, Am [1,2]. Thus, ISA is of significant importance in the definition of acceptance criteria and the safety assessment of LILW repository.

2. Experimental

The cement clinkers used in this study were obtained from ONDRAF/NIRAS and were used to prepare hydrated cement pastes (CEM I, CEM III, and CEM III + $CaCO_3$) under an Ar atmosphere. The protocol for the artificial pore solution was developed based on the compositional analysis of pore solution extracted from hydrated cement blocks. The details of the preparation and treatment of the cement pastes and pore solution can be found in [3]. The ISA stock was prepared by dissolving ISA lactone (obtained from Biosynth Carbosynth and Interchim) in a 1 M KOH + 1 M NaOH solution. To conduct the sorption experiment, ISA stock was added to the suspension of cement paste and artificial pore water solution with solid-to-liquid ratio (S:L) = 0.5 – 50 $g \cdot L^{-1}$ and 10^{-5} M < [ISA] < 0.13 M in HDPE vials. The phase separation was performed using membrane-syringe filtration (pore size: 0.45 µm). The filtrate was diluted with ultrapure HCl, and the non-purgable organic carbon was used to determine the remaining ISA after sorption in the solution.

3. Results and discussions

The sorption of ISA by cement was moderate, with a distribution coefficient (R_d) of 9 – 900 $L \cdot kg^{-1}$, which is in line with previous data [4]. The sorption capacity of cement paste was found to be similar to that of calcium silicate hydrate (C-S-H), suggesting that C-S-H is primary sorbing material for ISA in cement. The sorption data for lower ISA concentrations (< 10^{-2} M) followed a Langmuir-type isotherm, while for higher ISA concentrations, a steep increase in sorbed ISA on the cement solid phase was observed, which deviated from the Langmuir isotherm. This deviation was attributed to the possible precipitation of $Ca(ISA)_2(s)$, possibly as a surface precipitate. Furthermore, the interaction of cement pastes with ISA resulted in increased concentrations of Ca and Si with increasing ISA concentration. The preferential extraction of Ca over Si, indicating incongruent dissolution, could be explained by the formation of strong and stable complexes between Ca and ISA. Molecular dynamics (MD) simulations confirmed the key role of Ca as bridge between ISA and the C-S-H surface. The formation of a second surface complex hinted by MD at high ISA concentrations could be interpreted as a second sorption site in the C-S-H surface/HCP, a hypothesis proposed by other empirical models available in the literature.

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