

Uptake of Nb(V) by calcite and carbonated cement systems: impact of isosaccharinic acid and chloride

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Introduction

Niobium(V) is present in structural components in nuclear reactors. The isotope ⁹⁴Nb ($t_{1/2} = 2 \cdot 10^4$ a) is produced by neutron activation of natural ⁹³Nb during the operation of a nuclear reactor. ⁹⁴Nb is mostly present in streams resulting from the dismantling of nuclear power plants, as well as from the treatment of the primary cooling circuit, which may be disposed in cement-based repositories for low and intermediate level waste (L/ILW). Isosaccharinic acid (ISA) is a polyhydroxycarboxylic acid forming upon degradation of cellulose in hyperalkaline conditions. ISA is known to form strong complexes with hard Lewis acids, thus potentially affecting radionuclide retention in cementitious systems. High concentrations of stable chloride (up to $\approx 4\text{--}5$ M) have been also described for specific waste streams containing evaporator concentrates. This study focuses on the uptake of Nb(V) by calcite (CaCO_3) and carbonated cement systems in the absence and presence of ISA and chloride. Both materials are taken as representatives of the degradation stage IV of cement, with relevance to near-surface disposal systems.

Experimental

Sorption was investigated using a combination of ⁹³Nb (stable) and ⁹⁵Nb ($t_{1/2} = 34.97$ d) isotopes. Cement pastes (CEM I and III/C) were carbonated in closed reactors with a gas mixture CO_2 / N_2 of 30/70%. Batch sorption experiments were conducted in air at $T = 22$ °C, using calcite- and carbonated cement-equilibrated waters. Systems with $10^{-11} \text{ M} \leq [\text{Nb(V)}]_0 \leq 10^{-6} \text{ M}$ (as ⁹⁵Nb or ⁹³Nb + ⁹⁵Nb) with S/L = 1–10 g/L were investigated in the absence / presence of ISA ($1.0 \cdot 10^{-5} \text{ M} \leq [\text{ISA}] \leq 0.1 \text{ M}$) and chloride ($8.4 \cdot 10^{-5} \text{ M} \leq [\text{Cl}^-] \leq 2.0 \text{ M}$). The concentration of Nb(V) in the aqueous phase was quantified by gamma spectrometry after ultracentrifugation. Upper solubility limits of niobium were quantified with ⁹³Nb in the same pore water solutions used for sorption. Nb(V) solid phases and carbonated cement were characterized by XRD, BET and Raman. ⁹³Nb content in carbonated cement was quantified by alkaline fusion.

Results and discussion

The solubility of Nb(V) was quantified as $\sim 10^{-6}$ M at $t = 3$ days, but decreased to $\leq 10^{-8}$ M at longer equilibration times ($t = 13\text{--}121$ days). This solubility limit is significantly lower than the one calculated assuming a solubility-control by $\text{Nb}_2\text{O}_5(\text{cr})$. XRD and Raman support that a Ca-Nb(V)-OH solid phase is responsible for the solubility-control of Nb(V) under these conditions, although no thermodynamic data for such solid phases is currently selected in available thermodynamic databases.

In calcite systems, a moderate uptake at short contact times ($R_d \approx 10^3 \text{ dm}^3 \cdot \text{kg}^{-1}$ at $t = 3$ days) was followed by a steady increase of distribution ratios with time ($R_d > 2 \cdot 10^4 \text{ dm}^3 \cdot \text{kg}^{-1}$ at $t = 89$ days). These observations were explained by a fast adsorption, followed by the slow incorporation into the calcite structure. The stronger uptake observed for carbonated cement paste ($R_d \approx 10^6 \text{ dm}^3 \cdot \text{kg}^{-1}$) is attributed to the presence of amorphous phases with larger surface area, primarily $\text{SiO}_2(\text{am})$ and C-S-H with low Ca/Si. The formation of complexes with isosaccharinic acid (ISA) decreases Nb(V) uptake, although sorption remains strong up to $[\text{ISA}]_{\text{tot}} = 0.1$ M. Chloride has a minor effect on the uptake of Nb(V) up to $[\text{NaCl}] = 2$ M. This work provides a sound basis for the quantitative description and mechanistic understanding of ⁹⁴Nb retention in L/ILW repositories.

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