

Sorption of niobium(V) in cementitious conditions: mechanism and impact of isosaccharinic acid and chloride

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1. Introduction

Niobium (Nb) is present in structural components (e.g., Ni-based alloy and stainless steel) of nuclear reactors. The long-lived isotope ⁹⁴Nb (half-life: 20,000 years) is produced by the neutron activation of ⁹³Nb (naturally occurring and stable isotope). The waste stream containing ⁹⁴Nb is generated by the dismantlement of nuclear power plants and the treatment of primary coolant. ⁹⁴Nb may be one of the main contributors to the annual dose potentially mobilized from a low- and intermediate-level radioactive waste (LILW) repository. Nb is predominantly present in the pentavalent oxidation state in the aqueous system, i.e. Nb(V), whereas the trivalent oxidation state is exclusively expected under very acidic and extremely reducing conditions.

Cementitious materials (concrete, mortar, and grout) are extensively used in LILW disposal systems as structural materials, waste forms, and stabilization agents. The cement-based materials can be gradually degraded by contact with water, with the consequent evolution of pore water (PW) conditions at alkaline pH (10 < pH < 13.5). As cementitious materials have a high sorption capacity for metal ions, strong retention of Nb(V) by sorption on hardened cement pastes (HCP) is expected in a LILW repository system. However, previous sorption studies of Nb(V) by HCP showed a large discrepancy in sorption capacity (i.e., distribution coefficients, R_d) [1-4].

Isosaccharinic acid (ISA) is a polyhydroxycarboxylic acid generated by the degradation of cellulose in cementitious conditions. It has been reported that ISA can form strong and stable complexes with hard Lewis acids (e.g., plutonium [5], zirconium [6]), thus affecting the retention of radionuclides in cementitious systems of LILW repository. Also, conditions with high chloride concentrations have been described for a certain type of waste stream. This study investigates the sorption of Nb(V) on HCP and calcium silicate hydrate (CSH, one of the main hydrates in HCP). Besides, the impact of ISA and chloride (Cl⁻) on R_d is examined.

2. Experimental

CEM I, CEM III, and CEM III + CaCO₃ were produced by hydration of cement clinkers provided by ONDRAF/NIRAS under Ar atmosphere. The outer surface (≈ 3 mm) of the cement monolith was removed and the cement powder was prepared by crushing, milling, and sieving down to < 63 μ m. Artificial PW in CEM I system was prepared using a modified protocol of young cement PW [7], whereas the squeezed water from CEM III HCP was considered as a preliminary composition for PW. The final PW composition was determined by the equilibrium of preliminary PW and HCP powders of CEM III and CEM III + CaCO₃. CSH was prepared by mixing CaO, SiO₂, and purified water and equilibrated more than 2 weeks prior to use.

Sorption experiments described in this work were conducted using a combination of non-radioactive ⁹³Nb and radioactive Nb isotopes (mostly ^{91m,92m,95}Nb). The active Nb isotopes were obtained by the irradiation of zirconium (Zr) foil with natural isotopic abundance in a cyclotron operated at Helmholtz-Zentrum Dresden-Rossendorf in Leipzig for nuclear reaction ^{nat}Zr(*d,x*). The active Nb isotopes with trace concentrations were separated from the Zr matrix with combinational use of ion exchange resins [8,9].

ISA and chloride stock solutions were prepared by dissolving ISA lactone in 1 M KOH + 1 M NaOH solution and NaCl in the cement PW. The preparation of sorption samples was performed by adding Nb, ISA, and Cl stocks into suspensions of HCP + PW or CSH + PW with $3.5 \cdot 10^{-9} \text{ M} \leq [\text{Nb}] \leq 1 \cdot 10^{-4} \text{ M}$ and desired solid:liquid ratios (S:L) of $0.1 \text{ g} \cdot \text{L}^{-1} \leq \text{S:L} \leq 50 \text{ g} \cdot \text{L}^{-1}$. Thus, this work focuses on binary (HCP-Nb/HCP-ISA/HCP-Cl), ternary (HCP-Nb-ISA/HCP-Nb-Cl), and quaternary (HCP-Nb-ISA-Cl) sorption systems. The quantification of stable Nb, Ca, and Si was conducted by ICP-OES and ICP-MS. Gamma spectroscopy was used to quantify remaining active Nb isotopes in the aqueous phase after solid/liquid phase separation by ultrafiltration (4 kDa) and ultracentrifugation ($\approx 600,000 \times \text{g}$).

3. Results and discussions

3.1. Nb(V) sorption in the absence of ISA and Cl⁻

Nb(V) sorption by HCP and CSH is fast and the sorption equilibrium was attained after 5 days. The sorption is strong with $\log R_d = 5 - 6$ (R_d in $L \cdot kg^{-1}$). A linear sorption isotherm with slope ≈ 1 was obtained, indicating that R_d concept is valid to explain Nb(V) sorption by HCP in the wide range of [Nb].

3.2. Sorption mechanism

Inactive Nb contents in CEM I and CEM III were quantified as (3.1 ± 0.3) and (7.1 ± 0.7) ppm by using total dissolution by alkaline fusion and ICP-MS. Considering the ubiquitous Nb contents in HCP, isotopic exchange with stable ^{93}Nb may play a role in the uptake of active Nb isotopes ($^{91m,92m,95}Nb$ in this experimental work and ^{94}Nb in nuclear waste). Nevertheless, the uptake by CSH phases is proposed as the main sorption mechanism based on almost identical sorption isotherms of HCP and CSH, and the large inventory (50 – 60 %) of CSH in HCP.

3.3. Impact of ISA and Cl^- on Nb(V) sorption

ISA is moderately sorbed by HCP and weak sorption of Cl^- is observed. ISA significantly decreases Nb(V) sorption at $[ISA] > 10^{-3}$. Also, ISA incongruently dissolves HCP resulting the increase in [Ca] of PW. Thus, the formation of stable (Ca-)Nb(V)-ISA complexes and HCP dissolution by ISA may be the mechanisms of the ISA effect on the reduction Nb(V) sorption. On the other hand, the impact of Cl^- is not significant within the investigated range of [Cl].

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