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## **Influence of the redox state on the actinide sorption under highly alkaline conditions: batch sorption studies on titanium dioxide and calcium silicate hydrates**

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Cementitious materials are an important component in the multi-barrier concepts developed in many countries for the safe storage of low and intermediate level radioactive waste (L/ILW) in deep geological repositories. Reliable thermodynamic models able to predict the interaction between radionuclides and cementitious materials in the long term are important for the performance assessment of such repositories. Development of these models requires a sufficiently detailed macroscopic and molecular-level understanding of the uptake processes involved. Studies on the retention of radionuclides by cementitious materials have focused predominantly on adsorption as the relevant uptake process. However, recent spectroscopic studies performed in our laboratory, suggest that incorporation in calcium silicate hydrates (C-S-H) may contribute significantly to the radionuclide immobilization. C-S-H phases, the major constituent of hardened cement paste, are characterized by high recrystallisation rates making them an ideal system for the incorporation of radionuclides present in cement-based repositories.

In the present study, batch sorption experiments have been performed to investigate the effect of the redox state (+IV, +V, +VI) and aqueous speciation on the uptake of neptunium in cementitious systems under high pH conditions. Batch sorption experiments were carried out with C-S-H phases and titanium dioxide (TiO<sub>2</sub>), a solid phase stable under high pH conditions and often used as a model sorbent in surface complexation studies. Comparison of the sorption of the actinides on these two solids may allow the influence of incorporation processes on the immobilisation of actinides by C-S-H phases to be assessed.

Neptunium uptake was found to be fast and sorption distribution ratios (R<sub>d</sub> values) were high, indicating strong retention by all solids. The experimental data further indicate that the sorption of the Np(IV,V,VI) on both types of solids strongly depends on the degree of hydrolysis. On TiO<sub>2</sub>, R<sub>d</sub> values for Np(IV), Np(V) and Np(VI) are identical at pH = 10 and decrease with progressing hydrolysis in case of Np(V) and Np(VI). On C-S-H phases, R<sub>d</sub> values for the three redox states are also identical at pH = 10. While the R<sub>d</sub> values for Np(VI) sorption on C-S-H phases decrease with progressing hydrolysis, the R<sub>d</sub> values for Np(IV) and Np(V) sorption are not affected by the pH. In addition to the effect of hydrolysis, the presence of Ca is found to promote Np(V) and Np(VI) sorption on TiO<sub>2</sub> whereas on C-S-H phases, the present wet chemistry data do not give unambiguous evidence. Thus, the aqueous speciation appears to have a similar influence on the sorption of Np(IV,V,VI) on both types of solids. Batch sorption tests with Th(IV) and U(VI) on C-S-H phases confirmed the sorption behavior observed for Np(IV) and Np(VI). Desorption tests finally showed that the actinides sorption on C-S-H phases is reversible.

The observed sorption behavior of the actinides on TiO<sub>2</sub> and C-S-H phases is qualitatively explained by invoking inter-ligand electrostatic repulsion between OH groups in the coordination sphere of Np(V) and Np(VI). This mechanism was proposed earlier in the literature for the prediction of actinide complexation constants with inorganic ligands.

We conclude that the present actinide sorption data on C-S-H phases can be interpreted in line with a reversible sorption mechanism. The degree of hydrolysis of the actinide cations and the presence of Ca play a key role in the sorption process. Wet chemistry studies of the actinides uptake by C-S-H phases cannot provide clear evidences for incorporation processes.

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