



NP(V) COPRECIPITATION WITH CALCITE

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The actinide elements U, Np and Pu form oxo-cations ('actinyl-cations') in oxidizing aqueous environments. The environmental behaviour of the actinyl ions U(VI), Np(V) and Pu(V,VI) is to a large extent controlled by sorption reactions (adsorption, coprecipitation/structural incorporation) with minerals. We study the structural incorporation of Np(V) into the host mineral calcite by coprecipitation in mixed flow reactors under steady-state conditions at room temperature. In this way reaction rates and partitioning coefficients can be determined under varying conditions. Data indicate that the precipitation rate of calcite decreases in the presence of trace amounts of Np(V) (1 $\mu\text{mol/L}$) compared to Np-free conditions. The homogeneous partition coefficient is 1.5, which is significantly higher than for U(VI) (0.06 [1]). The local structural environment of incorporated Np(V) is characterized from the Np L3 EXAFS. Measurements are performed at the INE-Beamline at ANKA (Forschungszentrum Karlsruhe). Our data suggest that the Np(V)-ions occupy calcium lattice sites, but with two missing carbonate groups in the first coordination sphere. The two axial oxygen atoms of the linear neptunyl-ions are oriented towards these vacant sites. Consequently, only four carbonates are observed to coordinate the Np(V)-ion. Np-O and Np-C bond lengths (2,41Å, 3,34Å, respectively) indicate slight structural relaxation of the carbonate groups from their ideal sites. A similar structural model was reported for U(VI) incorporated into calcite [2]. At this stage we cannot explain the apparent higher affinity of Np(V) for calcite compared to U(VI), however.

[1] Reeder et al. (2001): Coprecipitation of Uranium(VI) with Calcite: XAFS, micro-XAS, and luminescence characterization, *Geochimica et Cosmochimica Acta* 65, 20 pp. 3491-3593.

[2] Kelly et al. (2003): Uranyl Incorporation in Natural Calcite, *Environmental Science and Technology* 37, pp 1284-1287.