



## **Neptunyl(V) coprecipitation with calcite, interfacial reactions studied with synchrotron x-ray radiation**

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In this experimental study a wide range of methods has been used to investigate processes leading to incorporation of neptunyl(V) ( $\text{NpO}_2^+$ ) cations into the calcite structure following surface sorption and upon coprecipitation.

As part of the investigation calcite surface properties were characterized over a wide range of pH and  $p(\text{CO}_2)$  conditions using zetapotential and in situ crystal truncation rod measurements. A detailed picture of surface charging phenomena and the corresponding molecular surface arrangement under varying solution conditions could be gained.

The  $\text{NpO}_2^+$  adsorption species on the calcite surface were investigated by means of room temperature and low temperature (15 K) EXAFS spectroscopy.  $\text{NpO}_2^+$  seems to adsorb at the calcite surface as an innersphere complex. Adsorption kinetic and desorption experiments indicate that even under calcite equilibrium conditions  $\text{NpO}_2^+$  might become incorporated into the calcite structure.

Upon coprecipitation from calcite supersaturated solutions  $\text{NpO}_2^+$  is readily incorporated into the calcite structure. Incorporation species were investigated using room temperature, low temperature (70 K), and polarization dependent EXAFS measurements, together with conventional powder XRD, NIR and Raman spectroscopy. The linear  $\text{NpO}_2^+$  molecule seems to substitute one calcium ion and two adjacent carbonate ions in the calcite structure. It is hence coordinated by four monodentate bound carbonate ions in the equatorial plane. Np - Np interactions have not been observed. Polarization dependent EXAFS measurements indicate, in agreement with NIR spectroscopic results, that the coordination polyhedron is a distorted tetragonal bipyramid. Powder XRD data indicates that  $\text{NpO}_2^+$  incorporation causes local distortion in the calcite lattice.