Trivalent actinide coprecipitation with calcite

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Structural incorporation of actinide elements into calcite and associated aqueous solid solution equilibria may play a major role for long term safety aspects of nuclear waste disposal in a deep geological formation. In particular predicting the evolution of a nuclear waste repository system over geological time-scales requires a sound understanding of the involved reaction mechanisms – including coprecipitation. This study was indented to develop a molecular level process understanding of actinide uptake during calcite formation from aqueous solution.

Coprecipitation experiments with Cm(III) were performed in a mixed flow-through reactor at ambient conditions (21˚C). Actinide containing calcite was formed onto calcite seed crystals (2 m^2/g, 7 m^2/L) under steady state conditions. Defined hydrodynamic conditions ensured that coprecipitation was surface reaction controlled (as opposed to diffusion/transport controlled). Further, since the composition of the aqueous solution was kept constant throughout the coprecipitation experiment, a homogenous Cm(III) containing calcite was synthezised (in contrast to free drift experiments). Coprecipitation conditions were varied over a supersaturation range of 0.6 $<$ log10(IAP/K) $<$ 1.3 and a pH range between 8.1 and 12.5. The aqueous Cm(III) concentration varied between 0.7 and 750 ppm;

A homogeneous Doerner-Hoskin partition coefficient was determined to be 800. Equivalent experiments with chemically homologous Eu(III) gave a partition coefficient of 1100. Comparable results have been found from coprecipitation experiments using single crystals. Although we did not observe a correlation between precipitation kinetics and partition coefficient , it is not clear whether the observed partitions coefficients actually represent equilibrium conditions. On going work is focused on coprecipitation near equilibrium.

Molecular level sorption mechanisms have been determined using time resolved laser fluorescence spectroscopy (TRLFS) and extended x-ray absorption spectroscopy (EXAFS). TRLFS spectra revealed the presence of 2 distinct incorporated Cm(III) species – Cm^{3+} and $CmOH^{2+}$ occupying a Ca^{2+} lattice site. TRLFS measurements at low temperature (18K) show a strong splitting of the fluorescence emission band. This is a clear indication that the incorporated Cm is occupying different energy states. Based on our data we can rule out a simple $2\ Ca^{2+} = Na^+ + Cm^{3+}$ coupled substitution. EXAFS measurements were performed on Nd(III) containing synthetic calcite. The EXAFS fit results, accounting for oxygen, carbon and second oxygen shell support the occupation of Nd^{3+} at the Ca lattice site. The data give an average first shell (Nd–O1) radius of 2.43(7) $\pm$ 0.02 Å and a coordination number of 7.1 $\pm$ 1.1. Fitting results indicate a second-shell (Nd–C) radius of 3.27(2) $\pm$ 0.04 Å, third shell(Nd–O2) radius 3.55(4) $\pm$ 0.05 Å. The corresponding shell radii in an ideal calcite structure indicate substantial lattice dilation around the Nd^{3+}. The large Debye–Waller factors for the first shell suggests a strong distortion around the Nd^{3+} or a distribution of Nd-O distances.

Cm(III) uptake by Calcite via coprecipitation has been quantified as a function of the chemical composition of the aqueous solution. Spectroscopic data (TRLFS & EXAFS) allowed to identify 2 Cm(II) species and suggest complex incorporation mechanisms.