

ACTINIDE COPRECIPITATION WITH CALCITE

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The disposal of high level nuclear waste in deep geologic formations poses major scientific and social challenges for the next decades, independently of political decisions to stop or continue the use of nuclear energy. Perhaps, one of the most critical issues is related to the long term safety of a nuclear waste repository system over extended periods of time (up to 10^6 years). There seems to be a consensus in the scientific community that long-term predictions regarding the geochemical evolution of a waste repository system should be guided by equilibrium thermodynamics and geochemical insights. Furthermore, a molecular-level process understanding can help improving the confidence in available data on radionuclide behaviour in the geosphere beyond a simple phenomenological description.

The transport of radionuclides from the waste repository to the biosphere will depend on the supply of (ground) water. Sorption reactions between dissolved radionuclides and minerals will to a large extent control the migration behaviour in such aqueous environments. Four molecular-level sorption mechanisms have been identified in recent years: (i) outer-sphere surface complexation (physisorption), (ii) inner-sphere surface complexation (chemisorption), (iii) ion exchange and (iv) structural incorporation. Adsorption and exchange phenomena (i-iii) and the associated molecular-level reaction mechanisms have been studied extensively in the past. Currently, the retention of actinides and fission products is thought to be primarily controlled (in laboratory time intervals) by ion exchange and adsorption reactions at external mineral surfaces. However, incorporation of radionuclides into the bulk structure of host minerals also represents a potentially efficient retention mechanism, the importance of which increases with the reaction progress time.

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 and spectroscopic studies have been performed with the trivalent actinides

Cm(III) and Am(III) as well as with the pentavalent actinide Np(V).

Cm(III) and Am(III) - Coprecipitation experiments with Cm(III) and Am(III) were performed in a mixed flow-through reactor at ambient conditions (21°C). Actinide containing calcite was formed onto calcite seed crystals (2 m²/g, 7 m²/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)/Am(III) containing calcite was synthesized (in contrast to free drift experiments). Coprecipitation conditions were varied over a supersaturation range of $0.6 < \log_{10}(IAP/K) < 1.3$ and a pH range between 8.1 and 12.5. The aqueous Cm(III)/Am(III) concentration varied between 0.3 and 376 nanomol/L;

A homogeneous Doerner-Hoskin partition coefficient was determined to be 800. Equivalent experiments with chemically homologous (non-radioactive) 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. Ongoing work is focused on co-precipitation near equilibrium.

Molecular level sorption/uptake mechanisms have been determined using time resolved laser fluorescence spectroscopy (TRLFS) and extended x-ray absorption spectroscopy (EXAFS) (figure 1). TRLFS spectra revealed the presence of 2 distinct incorporated Cm(III) species – Cm³⁺ and CmOH²⁺ occupying a Ca²⁺ 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. EXAFS measurements were performed on Nd(III) – a non-radioactive chemical homologue – and Am(III) containing synthetic calcite. The EXAFS fit results, accounting for oxygen, carbon and second oxygen shell support the occupation of Nd³⁺ / Am³⁺ 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 ± 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

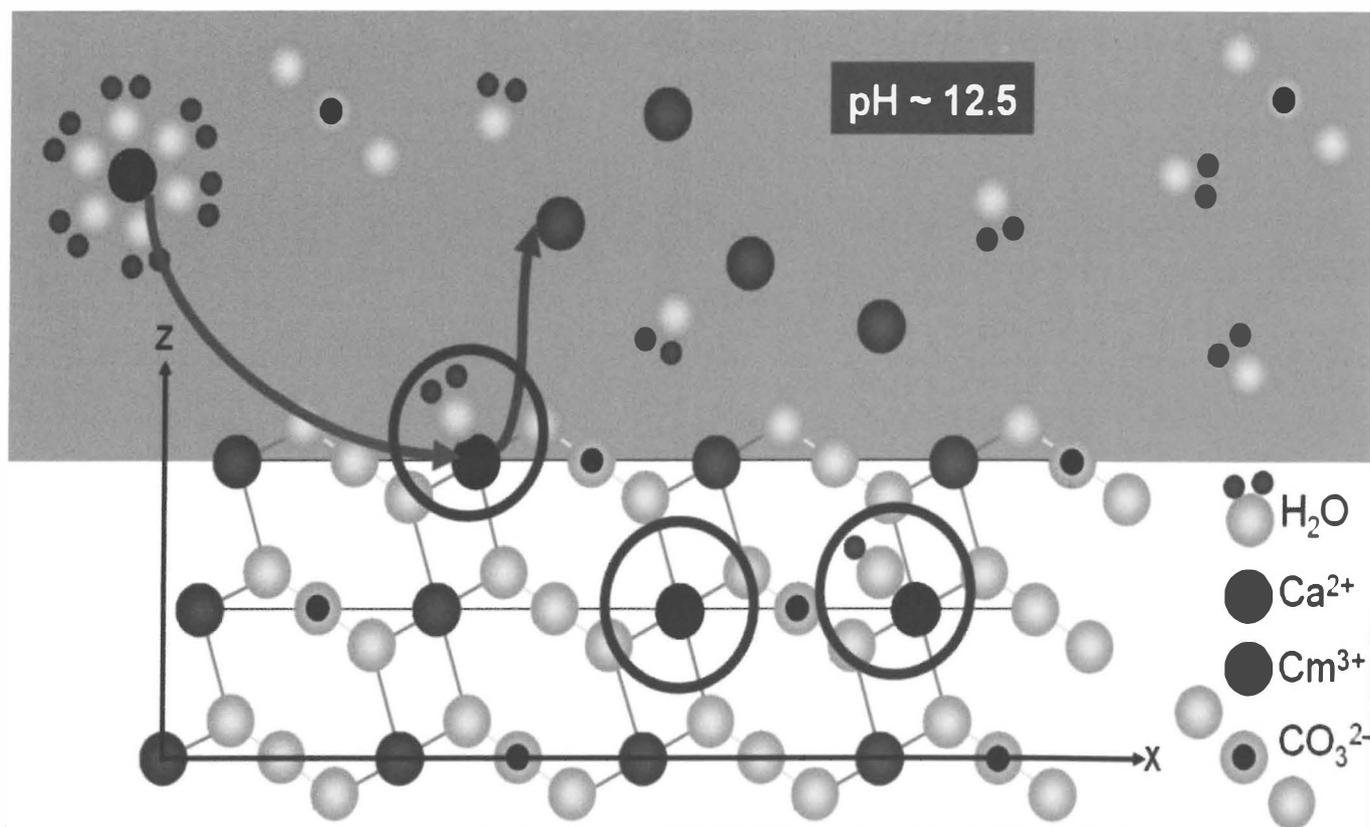


Figure 1: Structural model of the identified actinide species co-precipitated with calcite.

lattice dilation around the $\text{Nd}^{3+} / \text{Am}^{3+}$. The large Debye-Waller factors for the first shell suggests a strong distortion around the Nd^{3+} or a distribution of Nd-O distances.

Similar results have been obtained for Am(III) coprecipitated with calcite. The Am(III) L3 EXAFS spectra were recorded at the INE-Beamline at the ANKA synchrotron light source in Karlsruhe, Germany. The FT spectrum of the Am doped calcite samples exhibits a single low-R peak at $R \sim 1.8 \text{ \AA}$, which can be modeled as a single oxygen shell ($N = 6.3 \pm 0.6 \text{ O}$ at $2.40 \pm 0.01 \text{ \AA}$). This coordination number is much lower than the N which is found for the Am^{3+} aquo ion (8-9 oxygen atoms) and for Am sorbed onto mineral surfaces. In the case of Am(III) sorbed onto clay minerals like smectite and kaolinite the coordination number is found to be between 7 and 9. Further more the Am-O distance measured for Am in calcite is significant shorter than the distance which is found for $\text{Am}(\text{H}_2\text{O})_{8,9}$ (2.49 \AA) and which was detected for the Am/clay sorption species ($2.47 \text{ \AA} - 2.49 \text{ \AA}$). No shell splitting, as might be expected from the different TRLS species, is observed. As known from the TRLS data, the incorporated Am/calcite species is the predominant component in the system. We suggest that the signal of the Am/calcite sorption species is covered by the EXAFS signal of the dominating Am/calcite incorporation species. Furthermore, there is no Am-Am interaction, excluding the presence of separate Am mineral phases. The Am-O distance differs slightly from the Ca-O distance (2.36 \AA) in calcite but is in good agreement with structural parameters obtained in EXAFS studies on rare-earth element doped calcite (25, 26).

Np(V) - The actinide elements U, Np and Pu form oxocations ('actinyl-cations') in oxidizing aqueous

environments. Here, we have studied the structural incorporation of Np(V) into the host mineral calcite by coprecipitation. As a first step we try to prove that neptunyl-ions can be incorporated into the calcite crystal lattice. Further more, the uptake of Np(V) during coprecipitation was quantified in terms of a homogeneous Doerner-Hoskin partition coefficient.

Neptunium containing calcite samples were synthesised in a mixed-flow-through reactor at a pH of about 10.3, an SI(calcite) of about 1, a Np concentration of $1 \mu\text{mol/L}$ and an ionic strength of 0.1 M NaCl . As seed crystals we use Merck suprapur calcium carbonate with a diameter of $11-15 \mu\text{m}$ (sieved). The calcite surface area in the reactor was $\sim 0.2 \text{ m}^2$ (BET). The stock solutions were prepared with MilliQ water and Merck p.a. chemicals. Three stock solutions, the first containing the calcium, the second the carbonate and the third the neptunium were pumped continuously into the reactor. Calcium and neptunium concentrations were sampled before and after the reactor and analyzed by ICP-MS. In the reactor steady-state conditions were attained and the neptunium containing calcite grows homogeneously onto the seed crystals. From the concentrations, the mole balance $\Delta c (= c_{\text{in}} - c_{\text{out}})$ and the flowrate the reaction rate R and the homogeneous partitioning coefficient D could be calculated. The samples were examined by EXAFS measurements at the Np L3 edge (17.608 keV). The measurements were performed at the ANKA INE-Beamline in fluorescence-mode. As monochromator crystals we used Ge(422). The energy calibration was done by parallel measurement of a Zr-foil, defining the first inflection point as 17.998 keV . From each sample we recorded seven spectra from about 150 eV beneath the absorption edge up to 700 eV above the edge and analyzed the two resulting averaged spectra using Feff 8 and

	N	r [Å]	σ^2 [Å ²]
1 st shell O-yl	2 ¹⁾	1.8429 (0.0058)	0.0018 (0.0008)
2 nd shell O-carb1	4.08 (1.05)	2.4015 (0.0107)	0.0093 (0.0039)
3 rd shell C-carb	= N _{O-carb1}	3.2567 (0.0567)	0.0395 (0.0370)

Table 1: Results of the EXFAS fits. Coordination number N, interatomic distance r and Debye-Waller factors σ^2 (uncertainties in brackets) for the Np environment in calcite [¹, held constant during fit].

FEFFIT 2.54. Background removal was done with WinXAS 3.11.

Results from the mixed-flow-through reactor experiments show that in presence of Np the precipitation rate of calcite is significantly reduced compared to Np free conditions. The partitioning coefficient D (1.4±0.1) for neptunyl is significantly higher than the one reported for the structural equivalent uranyl (0.06). The results from the EXAFS fits are summarized in Table 2. From the fit results we conclude that the neptunyl-ions occupy calcium sites in the calcite lattice where two carbonates in the first coordination sphere are missing (see table 1: N_{O-carb1} is about 4 for V3 and V4, compared to 6 for Ca in calcite). The two axial oxygen atoms of the linear neptunyl-ions are likely oriented towards the resulting vacant Ca sites. The interatomic distances indicate structural relaxation of the remaining four carbonate groups from their ideal sites. A similar structural model was reported for U(VI) incorporated into calcite. The small Debye-Waller Factors, σ^2 , are evidence for the high order in this structure. A picture of the suggested structure is shown in figure 2.

This proposed structure leaves a charge excess of +3 in the calcite lattice. Up to now there is no evidence how this charge is balanced. Possible charge balancing mechanisms would be substitution of Ca²⁺ by Na⁺ or vacant Ca²⁺ sites. One possible reason for the apparently higher affinity of Np(V) to calcite compared to U(VI) could be that for the pentavalent neptunium this charge excess is only +3 while for the hexavalent uranium it is +4. Another reason could be the differing aquatic chemistry of Np and U. Under the chosen experimental conditions neptunyl forms a monocarbonate

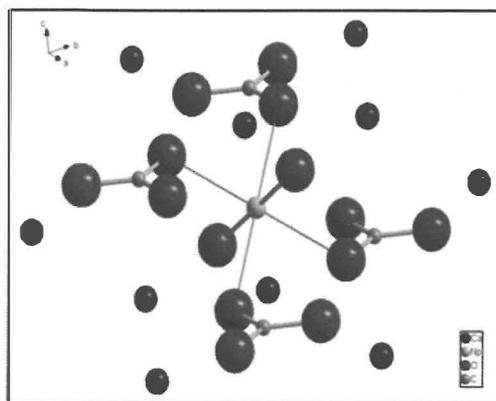


Figure 2: Structural model of neptunyl incorporated into calcite

complex, while uranyl is complexed by three carbonate-ions. This triscarbonatocomplex is less attracted to the forming calcite Surface because of its high negative charge.

In summary, it could be shown, that trivalent as well as pentavalent actinides can become structurally incorporated into calcite as a host mineral. Cm(III)/Am(III) have a high affinity for calcite ($D \sim 10^3$). Their incorporation involves two ionic species: An³⁺ and An(OH)²⁺, which occupy a Ca lattice site. However, the An³⁺ species seems to occupy several such Ca sites, which differ with respect to the local coordination sphere, quite likely related to structural defects as a consequence of the charge compensation. The contribution of the different species and sites to the overall co-precipitation reaction will be quantified. Without a doubt, in case of co-precipitation of trivalent actinides with calcite, modelling solid solution – aqueous solution equilibria without knowing the involved species and sites will yield incorrect thermodynamic data. Np(V) also seems to occupy a Ca lattice site within the calcite structure. However, due to the size and the actual geometry of the neptunyl ion, the local structure around an incorporated NpO₂⁺ ion differs to some extent from the calcite structure. This is also reflected by a significantly smaller partition coefficient $D \sim 1$. At this stage, we can not derive a molecular level substitution mechanism for Np(V) uptake.

Apparently, structural incorporation of tri- and pentavalent actinides into calcite involves rather complex heterovalent substitution mechanisms, which can only be identified by state of the art spectroscopic techniques combined with advanced synthesis methods.