Aquatic Chemistry and Thermodynamics of Actinides

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Introduction

The work performed at INE in a geochemically-based approach to the long-term safety analysis of final storage (see contribution about multi-barriers) focuses on nuclear fuels and on the transuranium elements, respectively, produced by neutron capture in the reactor. Chemically, these elements are part of the actinide series, i.e., the thorium, protactinium, uranium, neptunium, plutonium, americium, curium elements following after actinium, and seven other elements. Why this interest in actinides for an analysis of long-term safety? While the radiotoxicity potential of high-level radioactive waste arising from nuclear fission is dominated by the fission products (β- and γ-emitters) for roughly 300 years, Pu and the minor actinides (Np, Am, and Cm), and their disintegration products determine the potential over a period of hundreds of thousands of years. This is due to the longlived nuclides of the transuranium elements (e.g. Pu-239: 24,000 years) and the twenty times higher dose factor of α-emitters compared to β- and γ-emitters. As transuranium elements do not occur in nature in any sizable quantities, no direct knowledge exists of their geochemical behavior over geologic time periods, as is the case for stable elements. Another reason for focusing research at INE on actinides is seen in the fact that there are only very few institutions worldwide where transuranium elements can be handled.

In actinides, the 5f shell is filled up with electrons in an analogous way to the 4f shell of the lanthanides. While most lanthanides exist in the trivalent state, the lighter actinides have oxidation levels between III and VII, exhibiting a correspondingly complex chemical behavior. Figure 1 shows the known oxidation states of the light actinides and those which are stable in an aqueous medium. One characteristic of actinide chemistry are the dioxo cations with a linear O = An = O (An: actinide) structure which are present in the V-VI oxidation states, and the highly charged trivalent and tetravalent cations coordinating preferably with “hard” bases, such as F-, OH-, and CO$_3^{2-}$, through electrostatic interaction.

To quantify actinide releases from the repository in case of water ingress, and the migration of these actinides along an aqueous propagation path into the biosphere, the mobilizing and the immobilizing reactions must be considered. The former include dissolution, complexing, and colloid formation, while the latter comprise the precipitation of pure and secondary mixed phases as well as sorption onto mineral surfaces. The mobilizing reactions of tetravalent actinides will be discussed below for the example of ternary hydroxo-carbonate complexes. When discussing immobilizing reactions, a more detailed account will be given of sorption reactions as explained by the example of...

![Fig. 1: Familiar oxidation states (+3 to +7) of the light actinide ions and their respective electron configurations (i.e. numbers of 5f electrons). The oxidation states stable in an aqueous solution are shown in color. The chemical behavior of actinides in the geosphere depends primarily on the oxidation states present under the given geochemical conditions. The complexity of aquatic actinide chemistry is apparent from the large number of oxidation states, some of which exist side by side.](image-url)
laser spectroscopic examination of the boundary phase reactions of Cm(III) on sapphire single-crystal faces.

Geochemical modeling of actinides in systems related to repository conditions requires understanding aquatic chemistry and establishing a comprehensive thermodynamic database. Equilibrium constants for trivalent, pentavalent, and hexavalent actinides were elaborated for a broad range of boundary conditions of natural aquatic systems some time ago, especially also for concentrated brines of the type which can occur in a repository in salt formations.

A major gap in the thermodynamic database existed for the tetravalent actinides, for which only sparse and conflicting data were available even on such elementary reactions as hydrolysis. As a consequence, the chemical behavior of plutonium, which may exist in the III, IV, V, and VI oxidation states side by side in an aquatic system, cannot so far be described reliably in the environment. This lack of knowledge is due to the instability of highly charged ions in a not very acid or complexing medium. This results in the formation of polynuclear and colloidal solution species, respectively, and of sparingly soluble amorphous solid phases. Moreover, sensitive spectroscopic speciation techniques, which can be used very successfully, for instance, with Cm(III) (see contribution about spectroscopic speciation of actinides), are available for tetravalent actinides only to a limited extent.

In recent years, extensive studies have been carried out at INE of the solubility and hydrolysis of the tetravalent actinides (Th, U, Np, and Pu) and the formation and stability of eigen colloids. This resulted in a consistent description of the reactions occurring [1 - 3]; the thermodynamic data were incorporated into international databases [4]. In neutral and alkaline solutions, solubility is determined always by amorphous oxyhydroxides, An(OH)₄(am); compared to crystalline dioxides, AnO₂(cr), their solubility is six orders of magnitude higher. It was also seen that the generation of An(IV) eigen colloids, i.e. of dispersed An(OH)₄(am) particles in the nanometer range, increases solubility by several orders of magnitude. These colloids are in equilibrium with ionic species and were seen to be surprisingly stable in the neutral to alkaline pH ranges even at higher ionic strengths.

Other actinide reactions increasing solubility result from complexing with substances contained in the water, such as chloride, sulfate, carbonate, phosphate, and natural organic compounds (humic substances), etc. Carbonate plays a special role because of its strong complex formation with actinides and its omnipresence in all kinds of water. Trivalent and pentavalent actinides only generate binary complexes, An(CO₃)ₙ, under relevant conditions [4]. For tetravalent actinides, however, because of the much more pronounced tendency to hydrolyze, also the formation of numerous ternary complexes with hydroxide and carbonate can be assumed:

\[
\text{An}^{4+} + y \text{OH}^- + z \text{CO}_3^{2-} \rightleftharpoons \text{An(OH)}_{y}(\text{CO}_3)_{z}^{4-y-2z}
\]

As it is possible, under different boundary conditions, that two or more complexes always exist side by side, the complex stoichiometries and complexing constants, \( \log b_{1yz} \), as proposed in the literature, are mostly uncertain [4]. Any reliable description of complexing in the An(IV)-OH-CO₃ ternary system requires experiments in which the OH⁻ and CO₃²⁻ ligands are varied over the widest possible range. Studies performed with redox-stable Th(IV) are discussed below.

On the one hand, solubility experiments were carried out with Th(OH)₄(am) in 0.5 M NaHCO₃-NaCl solutions in a pH range of 4.5 – 7.5 in equilibrium with a CO₂ gas phase (open system). On the other hand, solubility in a closed system was studied in the pH range of 8.5 – 13.5 at constant total carbonate concentrations. Figure 2 shows the increase in solubility in carbonate solutions as against solutions containing no carbonate in open
and closed systems for the boundary conditions indicated.

The studies performed provide no indication of the formation of a carbonate-bearing solid phase; consequently, it may be assumed that Th(OH)$_4$(am) is the phase determining solubility. The solubility product and the hydrolysis constants of Th(IV) are well known from previous studies [1 - 3]. The shaded area in Fig. 1b illustrates the scattering of experimental data caused by contributions by incompletely separated Th(IV) colloids.

Simultaneous fitting of the complexing constants, log $\beta_{1yz}$, according to Equation 1, to the experimental series shown in Fig. 2 and to comparable data from the literature [5] indicated that the solubility data can be described unequivocally by relatively few complexes (solid lines in Fig. 2). The Th(OH)(CO$_3$)$_2^{2-}$ complex (log $\beta_{114}^{0} = 35.8 \pm 0.3$) dominates solubility at pH 8 – 11 (Fig. 2b). Below pCO$_2$ = 1 and 0.1 bar, in addition also the Th(OH)(CO$_3$)$_3^{2-}$ (log $\beta_{132}^{0} = 37.0 \pm 0.4$) complex becomes dominant. In addition, only Th(OH)$_2$(CO$_3$)$_2^2$, Th(OH)$_3$(CO$_3$)$^-$, and Th(OH)$_4$(CO$_3$)$_2^{2-}$ furnish significant, though less important, contributions to solubility. Other ternary complexes as well as pure carbonate complexes, Th(CO$_3$)$_{z}^{2z}$, do not play a role under these conditions. The complexing system in the Th(IV)-OH-CO$_3$ ternary system can be seen in Fig. 3. The two most important ternary complexes, Th(OH)(CO$_3$)$_{3}^{5-}$ and Th(OH)$_2$(CO$_3$)$_{2}^{2-}$, lie on a diagonal between the binary species, Th(OH)$_4$(am) (dominating at low carbonate concentrations above pH 5) and Th(OH)$_6$(am) (dominating at high carbonate concentrations [6]).

Analogous experiments are planned to derive corresponding complexes of Np(IV) and Pu(IV). The importance of ternary hydroxo-carbonate complexes compared to strictly binary complex species is relevant also to other complex ligands, such as humic substances, and takes a much greater effort in determining thermodynamic data than for

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Fig. 2: Solubility of Th(OH)$_4$(am) in a carbonate solution (I = 0.5 M, 22°C); (a) in the pH range of 3-8 at a CO$_2$ partial pressure, pCO$_2$ = 1.0 (blue), 0.1 bar (red) and, for comparison, carbonate-free (black); (b) in the pH range of 8-13.5 for total carbonate concentrations, (C$_{tot}$ = [HCO$_3$] + [CO$_3$$_2$$^-$]), of 0.1 (blue), 0.04 (red), and 0.015 M (green). Black squares in Fig. 2a: Solubility measurements by laser-induced breakdown detection (LIBD) under the exclusion of carbonate [1]; open squares in Fig. 2b: Östhols et al. [5]. The solid lines were obtained by simultaneous fitting of the experimental data, including the complexes mentioned in the text.
other actinide oxidation levels. The important finding of this study, namely that only very few mixed complexes out of the many possible ones are relevant, opens up a perspective for calculating the relative stabilities of complexes, and estimating them, respectively, in theoretical approaches. While the reactions discussed above determine the solubility and, hence, mobility of actinides in a given chemical environment, the interaction of actinides with mineral phases in the near and far fields of a repository in general results in retention or retarded transport. Most of these interactions so far have been described phenomenologically by a distribution coefficient, $K_D$, between the aqueous and the solid phases and taken into account in transport calculations. However, this sorption coefficient applies only to the given system and can be translated into other chemical boundary conditions only in a very limited way. Moreover, the $K_D$ value encompasses different sorption mechanisms, such as ion exchange, specific adsorption to functional groups on the mineral surface, and surface precipitation and incorporation in secondary phases, all of which may have very different sorption and desorption kinetics. Quantitative descriptions of sorption in the absence of any knowledge of the processes going on therefore appear to be not very reliable. Over the past few years, thermodynamics-based sorption models have increasingly been used, such as the surface complexing model (SCM), which covers a broad range of pH levels and concentrations. Model fitting of hypothetical surface complexes is achieved by distribution coefficients determined as a function of pH and concentrations of metal and sorbent.

To test the reliability of SCM in all its variants when applied to actinide ions of higher valencies, the sorption of Cm(III) onto model mineral phases (amorphous SiO$_2$, γ-Al$_2$O$_3$, clay minerals, etc.) was investigated by time-resolved laser fluorescence spectroscopy (TRLFS) [7, 8]. It was seen that this allows direct differentiation among sorption mechanisms, such as ion exchange in clay interlayers, specific adsorption onto aluminol groups of γ-Al$_2$O$_3$, and clay minerals, as well as the incorporation of non-hydrated Cm ions into alumosilicates (see contribution about speciation). Moreover, the pH-dependence not only permits the usual pH-edge to be determined but also a differentiation to be made among various ternary surface complexes. However, no information about the influence of heterogeneity of the binding sites and the interface potential, respectively, can be derived from sorption measurements of colloidal solid phases. Consequently, the studies were extended to single crystals with clearly defined crystal faces. Sapphire single crystals ($\alpha$-Al$_2$O$_3$) were chosen as a suitable, easily available substrate because of their favorable spec-
trosopic properties and their model character for the spectroscopically inaccessible iron oxides. Sapphire wafers with different orientations ((018), (104), (012), (110), (001)) were cleaned thoroughly and characterized by various techniques (XPS, AFM, LEED). The orientation of UO$_2^{2+}$ on the surface was determined by polarized X-ray absorption spectroscopy under a grazing angle of incidence (GI-XAFS) [9] while, for characterization of the functional alumino groups, sum frequency IR spectroscopy was used (see contribution about speciation). Some preliminary results about interface reactions of Cm(III) will be discussed below.

Sorption of a Cm solution of $6.5 \times 10^{-7}$ mol/l at pH 5.1 on the crystal faces of 1 cm$^2$ autoradiographically indicated a uniform cover, after two days of contact time, of 0.02 – 0.4 atoms/nm$^2$ for the different orientations. As is shown in Fig. 4, excellent emission spectra can still be obtained for a surface coverage of 0.2 – 2.0 % of the maximum binding capacity. Significant differences are found for Cm(III) on the (001) surface with respect to the peak position and fluorescence lifetime compared to the other four crystal surfaces, which have practically identical spectra and lifetimes. Analogous observations are obtained also by means of XPS. The quantity of Cm(III) sorbed strongly depends on the single-crystal faces. The highest sorption is found for the (001) surface, while the lowest sorption is found for the (018) orientation. Because of the very similar spectra for Cm(III) on the (001) surface and on colloidal $\gamma$-Al$_2$O$_3$ particles [4], the surface species can be assumed to be very similar. Most probably, they consist of $\gamma$-Al(OH)$_3$ formed on the surface as a result of contact with water [10]. This effect is much less pronounced for the other sapphire single-crystal surfaces. These preliminary results exhibit a large potential for obtaining fundamental insights into interface reactions by sensitive complementary spectroscopic methods.

![Fig. 4: Fluorescence emission spectra for Cm(III) sorbed at pH 5.1 to various sapphire single-crystal surfaces, (001), (110), (018), (012), and (104). The spectra have been normalized to identical peak heights. For comparison, the spectra are shown for free Cm$^{3+}$(aq) and for the first Cm(III) sorption species to $\gamma$-Al$_2$O$_3$ colloids [8].](image-url)
Outlook

INE plays a leading role internationally in the speciation and thermodynamics of aquatic actinides. Its findings are incorporated in thermodynamics databases and constitute the basis of geochemical and reactive transport modeling for safety analyses. The importance of this line of research is underlined by the European Network of Excellence for Actinide Sciences (ACTINET), which is currently being built up and will serve to revive the actinide sciences by opening research facilities to universities and train highly qualified young scientists. INE together with ITU\(^1\), SCK-CEN\(^2\), and CEA\(^3\) as the coordinator is one of the main players in this network.

\(^{1}\) ITU: Institute for Transuranium Elements
\(^{2}\) SCK-CEN: Studiecentrum voor Kernenergie / Centre d’Etude Nucléaire
\(^{3}\) CEA: Commissariat à l’Énergie Atomique

Literature


