

Solubility of actinides in complex solutions

(What are the solubility controlling phases in complex media?)

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During the past fifteen years, actinide solubility has been studied to determine the amount of radioelement available for migration from a possible waste disposal. Solubility studies is also used to obtain aqueous speciation in solutions equilibrated with well identified solid phases. In relatively simple chemical systems, an actinide cation is precipitated with an anion: OH^- , CO_3^{2-} or other hard cations available in groundwaters, typically phosphate, silicate or sulphate. These anions can also coprecipitate actinides with major cations: typically sodium, potassium, calcium, magnesium. In sufficiently old (thousand or ten thousand years) natural waters, speciation of dissolved mineral species is controlled by solubility, i.e. equilibrium between aqueous and solid phases. This is solubility definition.

When they are the result of weathering, Uranium and Thorium minerals in nature give indications on solid phases that can control solubility of actinides from a waste disposal. A great variety of these minerals is known. Uranium can be found at the +4 and +6 oxidation states in these solid phases and even in the same solid. Nevertheless solubility data are not available for all these solids and some of them need confirmation. Actinides at the same oxidation state are expected to form soluble or solid chemical species of the same stoichiometry, and of similar stability; but relative redox stabilities are different within the actinide series; hence different behaviour are finally expected for U, Np, Pu and Am.

Thermodynamic data (solubility products) are available for the following solid phases of transuranien elements: $\text{Pu}_2\text{O}_3(\text{cr})$, $\text{Am}_2\text{O}_3(\text{cr})$, $\text{Am}(\text{OH})_3(\text{s})$, $\text{AmOHCO}_3(\text{s})$, $\text{Am}_2\text{CO}_3(\text{s})$ and $\text{AmPO}_4(\text{am,hyd})$ for Pu(III) or Am(III), $\text{NpO}_2(\text{hyd,am})$, $\text{PuO}_2(\text{hyd,am})$, $\text{Pu}(\text{HPO}_4)_2(\text{am})$ for Np(IV) or Pu(IV), $\text{NpO}_2\text{OH}(\text{am})$ and $\text{Np}_2\text{O}_5(\text{cr})$ for Np(V). They were obtained from laboratory experiments: they could control solubility in ground waters; but other simple solids are known for Thorium Uranium and Lanthanides, and coprecipitation with major ions is anyhow rather expected in ground waters. Unfortunately the solubility products and eventually the stoichiometries are not available for such mixed solid phases including transuranien cations. An experimental effort is then needed to identify solid phases controlling the solubility of natural Actinides (Thorium and Uranium) and Lanthanides in existing ground waters, to check the interpretation by synthesising them in laboratory, this could also be a first step to prepare the corresponding Np(IV) Pu(IV), Am(III) and Cm(III) compounds.

In reducing near neutral media, $\text{PuO}_2(\text{am,hyd})$ solubility is very low, lower than $10^{-9} \text{ mol.l}^{-1}$: as for Uranium the dioxide could control Plutonium solubility in reducing ground waters. Surprisingly $\text{NpO}_2(\text{hyd,am})$ solubility is less low ($10^{-8.3} \text{ mol.l}^{-1}$), this values could be originated in the poor detection limit for ^{237}Np , or formation of polynuclear Np(IV) hydroxide.

The presentation is first focussed on methodology to measure solubility, based on experimental results for the "simple" system Np(V) in sodium carbonate / bicarbonate aqueous solutions. Solid solution and ionic exchanged on clayey mineral are also examined. For solid solution, empirical approaches are compared, including models minimising solubility as a function of stoichiometric coefficient within the solid. Mass action law in it usual form is not valid when stoichiometric coefficients are not constant, even neglecting the influence of activity coefficients. The hypothetical $\text{Na}_{2x-1}\text{NpO}_2(\text{CO}_3)_x$ solid solution would allow cationic exchange (hence $D = [\text{Na}^+] / [\text{NpO}_2^+] / (2x-1)$), mass action law is $((2-y) / [\text{Na}^+])^{2-y} / (x / [\text{NpO}_2^+])^y / [\text{CO}_3^{2-}] = K_1^t K_2^{1-t}$ for the solid solution (a similar formula is proposed in Michard 1989), where $y = 1/x$, $K_1 = (x_i K_{s_i})^{y_i} / (2-y_i)^{2-y_i}$, $t = (y - y_2)/(y_1 - y_2)$, and K_{s_i} is the solubility product for the stoichiometric compound $\text{Na}_{2x_i-1}\text{NpO}_2(\text{CO}_3)_{x_i}$. More complicated systems are then discussed, involving ligand competition (Am(III) / OH / CO_3) or redox reaction (Np(IV) or Pu(IV) solubility in bicarbonate, carbonate or acidic aqueous solutions). Finally indications are given on solid phases controlling Uranium solubility in typically Oklo ground waters.