Thermodynamic data for modelling actinide speciation in environmental waters

Pierre Vitorge, Hélène Capdevila

(1) CEA DEN/Saclay/DPC/SECR/LSRM, UMR 8587 (CEA-Université d’Evry-CNRS), 91191 Gif-sur-Yvette CEDEX, France.
(2) CEA DEN/Cadarache/DED/SAMRA/LCPC, 13108 Saint-Paul-lez-Durance CEDEX, France.

An operational TDB is generated from the validated NEA-TDB by adding formation constants (eventually those of chemical analogues, and typically $\log \beta^\circ_{\text{Pu(CO}_3\text{)}_5^{6-}} = 35.6$, $4 \text{pH}_{1/2} = -37.5$ for Np(VII) hydrolysis, possible maximum values for formation constants of several Pu(CO$_3$)$_i$(OH)$_{4-2i-j}$+ complexes, and solubility products for compounds of tentative stoichiometries MO$_{2+x}$ for M = U, Np, Pu and Am), and by estimating new numerical values (typically $E^\circ_\text{AmO}_2^{2+/AmO}_2^{+}) = 1.50$, $E^\circ_\text{AmO}_2^{+}/\text{Am}^{3+}) = 1.48$, $E^\circ_\text{Am}^{4+/Am}^{3+}) = 2.45$V/SHE). Beside checking the consistency of published experimental data, and performing sensitivity analysis of their interpretation as for any critical review work, activity coefficients and pH calibration also appeared to be critical. Dramatic decrease in aqueous Np(V) solubility is expected, when it is coprecipitated at trace concentration: solubility controlled by the hypothetical ideal solid solution Na$_{2x-1}$NpO$_2$(CO$_3$)$_x$(s) ($2 \geq x \geq 1$), is calculated by solving the set of two thermodynamic equations $[\text{Na}^{+}]^{2x-1} \cdot [\text{NpO}_2^{2-}][\text{CO}_3^{2-}]^x = K_{sx}$, together with $(2x-1)[\text{NpO}_2^{2-}]/[\text{Na}^{+}] = D$, where $K_{sx} = K_{s1}^2 (16 K_{s2}/27)^{x-1} (2-1/x)^{2x-1}$ /x, $K_{s1}$ and $K_{s2}$ are the solubility products of the end-member compounds, and $D = 27K_{s1}^2/(16 K_{s2})$ is the equilibrium constant for Ionic Exchange NpO$_2^2$/Na$^+$. Conversely, equilibrium constant, D, of any ionic exchange equilibrium can be interpreted as ratio of solubility products of end-member compounds (eventually surface compounds).