Thermodynamic data for modelling actinide speciation in environmental waters

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Abstract

An operational TDB is generated from the validated NEA-TDB by adding formation constants (eventually those of chemical analogues, and typically $\log\beta°_{Pu(CO_3)_5^{6-}}$ = 35.$_6$, 4 $pH_{1/2}$= -37.$_5$ for Np(VII) hydrolysis, possible maximum values for formation constants of several $Pu(CO_3)_i(OH)_j^{(4-2i-j)+}$ 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 $E°_{(AmO_2^{2+}/AmO_2^{+})}$ = 1.5$_0$, $E°_{(AmO_2^{+}/Am^{3+})}$ = 1.4$_8$, $E°_{(Am^{4+}/Am^{3+})}$ = 2.$_{49}$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 $[Na^+]^{2x-1}\ [NpO_2^+][CO_3^{2-}]^x = K_{sx}$, together with $(2x-1)[NpO_2^+]/[Na^+] = D$, where $K_{sx} = K_{s1}^{2-x}$ $(16\ K_{s2}/27)^{x-1}\ (2-1/x)^{2x-1}\ /x$, 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^+/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).

Introduction

The Thermodynamic DataBase (TDB) of Nuclear Energy Agency (NEA-OECD) [1, 2] reflects present quantitative knowledge, as limited by the available experimental information, and by theoretical models: sounded well-established and accepted thermodynamic descriptions of chemical systems are needed. NEA has validated a consistent set of data; when validation was not possible these critical reviews [2-6] provided qualitative information, and discussed not-selected numerical values. For describing actual chemical systems, it is needed to add (or at least to test) non-validated numbers, thus obtaining an operational TDB (**oTDB**). Qualitative information can typically be made semi-quantitative by estimating maximum possible values of formation constants, which can be accounted for, by performing statistical sensitivity analysis on their values for a given calculation, typically part of a performance assessment, outside the scope of the present paper. In the present paper, we outline a few key points: (i) Practical using of an existing validated TDB (building an oTDB). (ii) Selecting sets of thermodynamic values for systems reasonably well known, or conversely, when inconsistent experimental information is available. (iii) Possible extensions of thermodynamic descriptions to solid solutions (**SoS**), which will appear to encompass ionic exchange equilibria.

We already used an unpublished **oTDB** (Tab.1) to plot Pourbaix diagrams, and estimated possible thermodynamic stabilities of MO_{2+x} for M = U, Np, Pu and Am [7], keeping consistency with the NEA-TDB (by using the same methodologies, auxiliary values and ionic strength, **I**, corrections), and using analogies. This selection of data and corresponding discussion are in Tab.1 and in its the footnotes.

We illustrate the **selection of complexing and solubility data** for Np(V) in CO_3^{2-}/HCO_3^- aqueous media, a system for which a sufficient set of thermodynamic data have been validated [6]. Conversely, a range of possible complexes of the form $Pu(CO_3)_i(OH)_j^{(4-2i-j)+}$ has been suggested; but there is not enough reliable experimental information for selecting their possible thermodynamic stabilities [6]. As a consequence, in typical environmental conditions (pH = 7, 10^{-3} mol.L^{-1} $[HCO_3]_{total}$) inconsistent solubilities of Pu(IV) are calculated: 10^{-3} to 10^{-10} mol.L^{-1} from equilibrium constants published in Ref.[8] and [9 or 10], respectively. For handling this inconsistency, we will estimate maximum possible values of formation constants, based on recent experimental data [10] published too late to be included in Ref.[6]. A similar experimental work on Np(IV) was published [11a], and used in Ref.[6]. We will use here the same methodology for Pu, keeping consistency with our stepwise constant k_5, and the corresponding I corrections for the $Pu(CO_3)_4^{4-}/Pu(CO_3)_5^{6-}$ equilibrium [12], as validated in Ref.[6].

Finally we propose formula to extend thermodynamic descriptions (hence corresponding TDB) to

aqueous solubilities controlled by solid solutions (SoS). Semi-empirical models for describing several natural processes are still under debate as typically coprecipitation, sorption on minerals or colloids, complexation by natural organic matters. A logical first step is the thermodynamic ideal description, before eventually adding empirical formula (*i.e.* for non-ideal SoS outside the scope of the present paper). However, thermodynamic description for ideal SoS was recently proposed [7, 13], we shall adapt it to Np(V) aqueous solubility, and compare with the experimental results reported in the first part of this paper. The dissolution reaction of the SoS (where y = 1/x) in an aqueous solution:

$$Na_{2-y}(NpO_2)_yCO_3(s) \leftrightarrows (2-y)Na^+ + y\ NpO_2^+ + CO_3^{2-} \qquad (1)$$

actually includes the corresponding Na^+/NpO_2^+ Ionic Exchange reaction:

$$Na^+ + \overline{NpO_2^+} \leftrightarrows NpO_2^+ + \overline{Na^+} \qquad (2)$$

since varying only y (*i.e.* at constant $[CO_3^{2-}]$) in Eq.1 results in Eq.2. The upperlined species are in the SoS. The equilibrium constant

$$D = \frac{[NpO_2^+]\ [\overline{Na^+}]}{[Na^+]\ [\overline{NpO_2^+}]} \qquad (3)$$

is Mass Action Law (**MAL**) for Eq.2. For convenience, we use χ_X, the mole fraction of X in the SoS, as concentration unit for $[\overline{X}]$. However MAL for Eq.1 has a different form, because stoichiometric coefficients vary (through y in Eq.1), while deriving ΔG (for minimizing it) is used to demonstrate MAL. We shall propose a demonstration of the new form of MAL for Eq.(1), that will evidence both Eq.1 and 2 must be treated simultaneously. For consistency, the solubility products of the end-member compounds must be linked to the thermodynamic constants of the SoS [14a], despite the end-member compounds are not simultaneously stable, when the SoS is stable [14b].

Experimental details

For **Np(V) experimental solubilities in HCO_3^-/CO_3^{2-}** 3M $NaClO_4$ aqueous solutions, ^{237}Np was counted by γ spectrometry at 29 keV with a pure Ge detector. The detection limit was just below the lowest solubility shown in Fig.1. The reference compartment of the combined glass electrode was filled with a 3M $NaClO_4$ aqueous solution, where solid AgCl was added. Its slope was checked with 3 commercial pH buffers at I = 0.1M: in the range $3 < -\log[H^+] < 10$ it was within 98.5-99.6% of the theoretical value (59.16 mV/log unit at 25°C). It was calibrated with I = 3M $NaClO_4$ solutions: (i) 0.01M $HClO_4$ ($-\log[H^+] = 2$), (ii) 0.1M HCO_3^-/1 atm carbonic gas partial pressure, P_{CO_2} ($-\log[H^+] = 6.99$), and (iii) 0.05M HCO_3^-/0.05M CO_3^{2-} ($-\log[H^+] = 9.62$) as proposed by Grenthe [2b]. The reproducibility of the measurements was within 0.06 $\log[H^+]$ unit. Experimental solubilities, X-ray diffraction patterns (of samples after solubility equilibration) and treatment of the data were given elsewhere [15], see also the caption of Fig.1.

The other Np(V) experimental solubilities were used as published [16, 17], and were already reviewed [6, 15]: pH calibrations were different in Ref.[15] and [17], due to different auxiliary data ($CO_2(g)/CO_3^{2-}$ equilibrium constant), and possibly (in Ref.[17]) junction potential. The solid phases were also possibly different in these two studies. However, in Ref.[17] it was not clear, whether the X-ray diffraction patterns were those of the solid phase, before or after solubility equilibria were achieved.

Solubility of PuO_2(am,hyd) [8-10 and 18] **and spectrophotometry of Pu(IV)** [12] **data in HCO_3^-/CO_3^{2-}** were used as published (some details are given in the caption of Fig.2). The data from Ref.[8] were discarded, since they probably were a partial publication of Report [18]. The solubility data from Ref.[8, 9 and 18] were considered [6] to be poorly reliable due to possible oxidation of Pu(IV) in the aqueous phase. Indeed, at least some of the Pu solubility data reported in Ref.[8 and 18] had certainly been in contact with the air: pH and P_{CO_2} were measured with specific electrodes, from these results (slope 2 in Fig.2a) we calculated $P_{CO_2} = 10^{-3.9}$atm at pH < 9 consistent with equilibrium with air, and $P_{CO_2} = 10^{-6.0}$atm at pH > 9.5 consistent with P_{CO_2} originated in Na_2CO_3 dissolution protected from the air (Na_2CO_3 is not a pH buffer). Between these two domains of pH conditions, pH controlled by $NaHCO_3$ dissolution (vertical lines in Fig.2a) can be inferred with no indication for possible contact with the air, since $NaHCO_3$ is a pH buffer. We discarded the data of too low total carbonate concentrations: aqueous speciations were not reliable, and Pu(IV) carbonate complexation is certainly negligible in these conditions. The corresponding solubilities were even more scattered than in Fig.2b.

Treatment of data and notations

When a chemical equilibrium cannot be directly studied in laboratory condtions, typically because it is too slow at 25℃, we calculated the corresponding equilibrium constant (**Tab.1**) from standard Gibbs energies of formation ($kJ.mol^{-1}$) at 25℃ [2-6]: $\Delta_fG(M(s)$, M = U, Np, Pu, Am) = 0, $\Delta_fG(U^{3+}) = -476.473$, $\Delta_fG(Pu^{3+}) = -578.984$, $\Delta_fG(Np^{3+}) = -598.698$, $\Delta_fG(Np^{4+}) = -491.774$, $\Delta_fG(UO_3.2H_2O(cr)$, Shoepite) = -1636.51, $\Delta_fG(UO_{2.67}(s)) = -1123.157$, $\Delta_fG(UO_{2.33}(s)) = -1080.572$, $\Delta_fG(UO_{2.25}(s)) = -1069.125$, $\Delta_fG(H_2O(l)) = -237.14$, $\Delta_fG(H_2(g)) = 0$ (reference state for hydrogen) and $\Delta_fG(H^+(aq)) = 0$.

We omitted notation (aq) for ions: for simplicity we typically wrote Pu^{3+} instead of $Pu^{3+}(aq)$. Typically, since Pu(s) reduces water, $\Delta_fG(Pu^{3+})$ was not directly measured. $\Delta_fG(Pu^{3+})$ corresponds to Reaction $Pu(s) \rightarrow Pu^{3+}(aq) + 3e^-$ (or equivalently $Pu(s) + 3H^+(aq) \rightarrow Pu^{3+}(aq) + 1.5H_2(g)$), where all the species are in the standard state (*i.e.* the molal activity of $Pu^{3+}(aq)$ is 1). However, these usual notations are not convenient (and actually not used) when handling Pu^{3+} in gas phase as typically studied with ab initio calculations. Nevertheless, in this paper we omit notation "(aq)" for simplicity. Notation "$\rightarrow$" in typically $Pu(s) \rightarrow Pu^{3+}(aq) + 3e^-$ is to stress the convention Δ_fG correspond to product minus reactant. A more usual convention is "$\leftrightarrows$" for stressing equilibrium is achieved. Following the SHE convention, the corresponding Gibbs energy for Reaction $H^+ + e^- \rightarrow 0.5H_2(g)$ (the definition for Notation e^-, of the electrochemists) is $0 = \Delta_rG(SHE) = 0.5\Delta_fG(H_2(g)) - \Delta_fG(H^+) - \Delta_fG(e^-)$, hence $\Delta_fG(e^-) = 0$ $kJ.mol^{-1}$ [19].

Aqueous speciations in HCO_3^-/CO_3^{2-} solutions are determined by 2 parameters (among $[CO_3^{2-}]$, $[HCO_3^-]$, pH, P_{CO_2}...) and not only one (Fig.2a). However, the Np(V) solubility results reported in Fig.1 appeared to be correlated only to $[CO_3^{2-}]$, this is consistent with the (relatively low) stability of Np(V) hydroxides [6], and it was also shown, that no Np(V) soluble polymer is formed in these conditions [6, 15].

Solubility of Np(V) was calculated as

$$[Np(V)]_t = [NpO_2^+]\ \alpha \tag{4}$$

$$\alpha = \sum_{i=0}^{3} \beta_i\ [CO_3^{2-}]^i \tag{5}$$

$$\beta_i = [NpO_2(CO_3)_i^{1-2i}]/([CO_3^{2-}]^i\ [NpO_2^+]) \tag{6}$$

$$[NpO_2^+] = K_{sa}\ /([Na^+]^{2a-1}\ [CO_3^{2-}]^a) \tag{7}$$

for a = 1 or 2. $\beta_0 = 1$. Aqueous speciations controlled by $NaNpO_2(CO_3)(s)$ are the mixed dashed lines (Fig.1) of equations

$$\log[NpO_2(CO_3)_i^{1-2i}] = \log K_{s1}\beta_i + (i-1)\log[CO_3^{2-}] \tag{8}$$

PuO_2(am,hyd) solubility was calculated similarly

$$[Pu(IV)]_t = \sum_{i,j} K_{si,j}\ [CO_3^{2-}]^i\ [OH^-]^{j-4} \tag{9}$$

$$K_{si,j} = [Pu(CO_3)_i(OH)_j^{(4-2i-j)+}]\ [OH^-]^{4-j}\ /[CO_3^{2-}]^i \tag{10}$$

$K_{s0,0}$ is the solubility product for the compound of stoichiometry PuO_2 controlling the solubility, $K_{si,j} = K_{s0,0}\ \beta_{i,j}$, where $\beta_{i,j} = [Pu(CO_3)_i(OH)_j^{(4-2i-j)+}]/([CO_3^{2-}]^i\ [OH^-]^j\ [Pu^{4+}])$.

Ionic strength (I) corrections were calculated from molal activity coefficients γ_X, of ions X^z, of charge z:

$$\log \gamma_X = -z^2\ D_{DH} + \varepsilon(X^z,M)\ m_M \tag{11}$$

and with the values of $\varepsilon(X^z,M)$ tabulated or estimated as explained in Ref.[6] (see also the caption of Tab.2). $D_{DH} = \frac{0.509\sqrt{I_m}}{1+1.5\sqrt{I_m}}$, I_m is molal I, p (= m/M) is the molar ($M = mol.L^{-1}$) to molal ($m = mol.kg^{-1}$) conversion coefficient [6]. K° is the value of Molar Equilibrium Constant K, in standard conditions (25℃, $I_m = 0$). From Eq.11

$$\log K° = \log K + \Delta n \log p - \Delta z^2\ D_{DH} + \Delta\varepsilon\ m + \Delta n_{H_2O} \log a_{H_2O} \tag{12}$$

where Δn is the algebraic sum of the stoichiometric coefficients. Typically for $K_{si,j}$ and $\beta_{i,j}$, $\Delta z^2 = (4-2i-j)^2+4-j-4i$, and $(4-2i-j)^2-j-4i-16$ respectively, and $\Delta\varepsilon_{si,j} = \varepsilon(Pu(CO_3)_i(OH)_j^{(4-2i-j)+},M) + (4-j)\varepsilon(OH^-,Na^+) - i\ \varepsilon(CO_3^{2-},Na^+)$ and $\Delta\varepsilon_{i,j} = \varepsilon(Pu(CO_3)_i(OH)_j^{(4-2i-j)+},M) - j\ \varepsilon(OH^-,Na^+) - i\ \varepsilon(CO_3^{2-},Na^+) - \varepsilon(Pu^{4+},ClO_4^-)$, where in $\varepsilon(X^z,M)$, $M = ClO_4^-$ or Na^+, when $z > 0$ or $z < 0$, respectively.

Solubilities controlled by solid solutions (SoS) were calculated by re-demonstrating Mass Action Law (**MAL**). Since stoichiometric coefficients in Eq.1 are not constant, the usual form of MAL is not valid [20], because its demonstration involves derivation: Eq.13. Let us first recall MAL for dissolution equilibria of a stoichiometric compound; it includes the following steps:

$$dn_i = \nu_i \, d\xi \qquad (13)$$

$$0 = \sum_i \mu_i \, dn_i = \left(\sum_i \nu_i \, \mu_i\right) d\xi = (\Delta_r G + R\,T \ln K) d\xi \qquad (14)$$

where, ξ is the *advancement variable* for the chemical reaction, n_i the number of moles of species i, of chemical potential μ_i and activity a_i, whose definition is $\ln a_i = (\mu_i - \mu°_i)/(R\,T)$, stoichiometric coefficients $\nu_i < 0$ for reactants and $\nu_i > 0$ for products (typically for Eq.1 $\sum_i \nu_i \, \mu_i = (2\text{-}y)\mu_{Na^+} + y\,\mu_{NpO_2^+} + \mu_{CO_3^{2-}}$), $\Delta_r G$ is the Gibbs energy of the reaction, and K its equilibrium constant

$$\Delta_r G = \sum_i \nu_i \, \mu°_i = -R\,T \ln K \qquad (15)$$

$$\ln K = \sum_i \nu_i \ln a_i \qquad (16)$$

Eq.16 is MAL. Typically for Eq.1 $\sum_i \nu_i \, \mu°_i = (2\text{-}y)\mu°_{Na^+} + y\,\mu°_{NpO_2^+} + \mu°_{CO_3^{2-}}$. When now ν_i's vary as a function of y (Eq.1), Eq.13 is no more correct [20], because n_i's are functions of both variables ξ and y (and not of the only variable ξ at constant y value as in Eq.13). For this reason Eq.13 is no more valid, it can now be written:

$$dn_i = \nu_i \, d\xi + \left(\frac{\partial n_i}{\partial y}\right)_\xi dy = \nu_i \, d\xi + \xi \frac{d\nu_i}{dy} dy \qquad (17)$$

This change is reported in the classical demonstration of MAL. We do not give all the details of these calculations, since it will appear the final results are two formula (Eq.21 and 22) already independently published [14a]: we will essentially show that these two formula must be solved simultaneously (not independently). Eq.14 now writes

$$0 = \left(\sum_i \nu_i \, \mu_i\right) d\xi + \xi \left(\sum_i \frac{d\nu_i}{dy} \mu_i\right) dy \qquad (18)$$

Since ξ and y are independent variables, each term is 0 in Eq.18. Now in Eq.15 and 16 μ_i is changed for $\delta_i = (\mu_i - \mu_{si})$ and a_i for a_i/a_{si}, respectively, where μ_{si} and a_{si} are the chemical potential and the activity, respectively of species i, in the SoS. They were constant and implicitly included in K (and $\Delta_r G$) in Eq.16 (and 15); this is no more possible since χ_X's now vary, as a consequence a_{si} and μ_{si} also vary; for this reason, they must be explicitly written. For $Na_{2-y}(NpO_2)_yCO_3(s)$ dissolution reaction (Eq.1) the two equations obtained from terms $d\xi$ and dy in Eq.18 are:

$$0 = (2\text{-}y)\delta_{Na^+} + y\,\delta_{NpO_2^+} + \delta_{CO_3^{2-}} \qquad (19)$$

$$0 = -\delta_{Na^+} + \delta_{NpO_2^+}, \qquad (20)$$

respectively. Eq.19 will clearly give formula similar to Eq.15. Using $\chi_{Na^+} = 2\text{-}y$, $\chi_{NpO_2^+} = y$ and $\chi_{CO_3^{2-}} = 1$, and comparing the reference states [14a] in the ideal (activity = concentration) SoS and end-member compounds of stoichiometries x = 1 and 2, Eq.19 leads to

$$\begin{aligned} K_{sx} &= [Na^+]^{2x-1} [NpO_2^+][CO_3^{2-}]^x \\ &= (K_{s1}^2/K_{s2})(K_{s2}/K_{s1})^x \,(16/27)^{x-1}\,(2-1/x)^{2x-1}/x \qquad (21) \end{aligned}$$

the new form of MAL for Eq.1. Similarly, from Eq.20 the classical form of MAL is obtained for Eq.2 [14a]:

$$D = (2x-1)[NpO_2^+]/[Na^+] = 27\,K_{s1}^2/(16\,K_{s2}) \qquad (22)$$

which is Eq.3 for ideal systems. The stoichiometric coefficients in Eq.2 (and 19) appear to be the derivatives (as a function of y = 1/x) of those in Eq.1 (and 20, respectively). This is a consequence of Eq.17. Similarly, "log(Eq.22)" is the derivative (as a function of y) of "log(Eq.21)", *i.e.* "log(Eq.22)" is obtained by taking the log of each member of Eq.21, substituting x = 1/y and deriving. Alternatively, Eq.21 and Eq.22 could have been directly obtained by equalising chemical potentials in both phases [14]:

$$[Na^+][NpO_2^+][CO_3^{2-}] = K_{s1}\,a_{s1} = K_{s1}\,(2\text{-}y)\,y \qquad (23)$$

$$[Na^+]^3\,[NpO_2^+][CO_3^{2-}]^2 = K_{s2}\,(a_{s0.5})^2 = K_{s2}\,((2\text{-}y)/1.5)^3\,y/0.5 \qquad (24)$$

where a_{s1} and $a_{s0.5}$ are the activities of the end-member compounds, when included in the SoS. Eq.23 and 24 can be deduced by linear combinations from Eq.21 and 22, and conversely. Eq.18 demonstrates that a set of two formula must simultaneously be solved, and facilitates using activity coefficients of individual ions, as based on statistical physics even in SoS [21]. Linear combinations also lead to terms K_{s1}^2/K_{s2} or K_{s2}/K_{s1} (in Eq.21 and 22), or K_{s2}/K_{s1}^3. Typically:

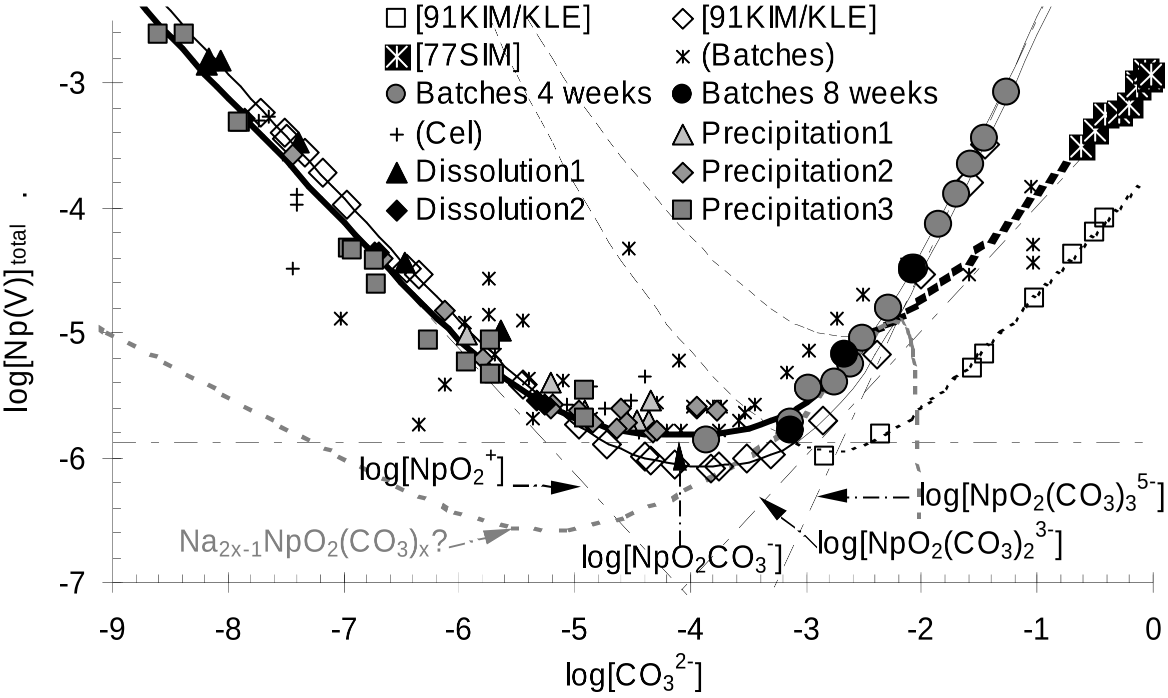

Fig.1: Np(V) solubility in CO_3^{2-}/HCO_3^- 3M $NaClO_4$ aqueous solutions at room temperature: *[77SIM] and [91KIM/KLE] are Ref.[16 and 17], respectively. The other data [15] were measured in $NaHCO_3$ or Na_2CO_3 closed batches, or as proposed by I.Grenthe [2b] under bubbling $CO_2(g)/N_2(g)$ mixtures (Cell) during several titrations and back titrations resulting in a series of precipitations / dissolutions. Small symbols (+, *) stress, the authors a priori excluded experimental data, where equilibrium conditions were not obtained. Bolded lines were calculated (Eq.4) with $\log\beta_1 = 5.25$, $\log\beta_2 = 8.15$ and $\log\beta_3 = 10.64$, and $\log K_{s1} = -10.65$ and (doted line) $\log K_{s2} = -12.10$ for the solids of stoichiometries $NaNpO_2CO_3$ and $Na_3NpO_2(CO_3)_2$, respectively. The other thin lines were fitted on the corresponding data [15]. The solubility of the ideal solid solution $Na_{2x-1}NpO_2(CO_3)_x(s)$ (grey doted line), is calculated by solving the set of Eq.21 and 22, assuming the end-members are the two above stoichiometric compounds (x = 1 and 2), see also Fig.3.*

$$K_{s2}/K_{s1} = [Na^+]^2_{1/2}\,[CO_3^{2-}]_{1/2} \qquad (25)$$

is the constant of Equilibrium

$$NaNpO_2CO_3(s) + 2\,Na^+ + CO_3^{2-} \leftrightarrows Na_3NpO_2(CO_3)_2(s) \qquad (26)$$

We used subscript $_{1/2}$ to stress Eq.25 is only valid, when two stoichiometric compounds are simultaneously stable: in those conditions the SoS is not stable. From Eq.22 and 25

$$x = ([Na^+]/[Na^+]_{1,2})\sqrt{[CO_3^{2-}]/[CO_3^{2-}]_{1,2}} \qquad (27)$$

We used Eq.4, 10, 21 and 22 to plot the curves in Fig.1, 2 and 3.

Results and discussion

Experimental solubilities of Np(V) in CO_3^{2-}/HCO_3^- aqueous solutions measured in different laboratories are reasonably consistent (Fig.1). This was used to validate Np(V) solubility products and complexing constants, together with other experimental results at different I (not shown here for clarity) [6]. The log-log plot in Fig.1 illustrates that MAL is valid over several orders of magnitude of concentrations. Nevertheless, critical reviewing revealed differences in the solid phases, and in pH calibrations [6], problems often encountered, when comparing solution chemistry data from different laboratories. X-ray results were tentatively interpreted by $NpO_2^+/Na^+(2H_2O)$ ion exchange in solid phases $Na_{2x-1}NpO_2(CO_3)_x(s)$ [15 and references cited therein] (see below).

Pu(IV) experimental solubilities in CO_3^{2-}/HCO_3^- aqueous solutions are scattered (Fig.2b) whatever the graphical representation used, and controversial interpretations were published: it cannot be reliable to extract thermodynamic data from such scattered experimental results. Despite possible contact with the air, that would oxidise aqueous Pu (see Section Experimental details), we tentatively interpreted as reflecting Pu(IV) solubility, those results in Ref.[18] we assumed to be in Na_2CO_3 or $NaHCO_3$ aqueous solutions. Complexes $M(CO_3)_5^{6-}$, $M(CO_3)_4^{4-}$ and $M(OH)_4(aq)$ are enough to account for available experimental solubilities of actinides(IV) (for M = Pu see typically Ref.[6, 12 and 22]) assuming some of the measurements did not reflect

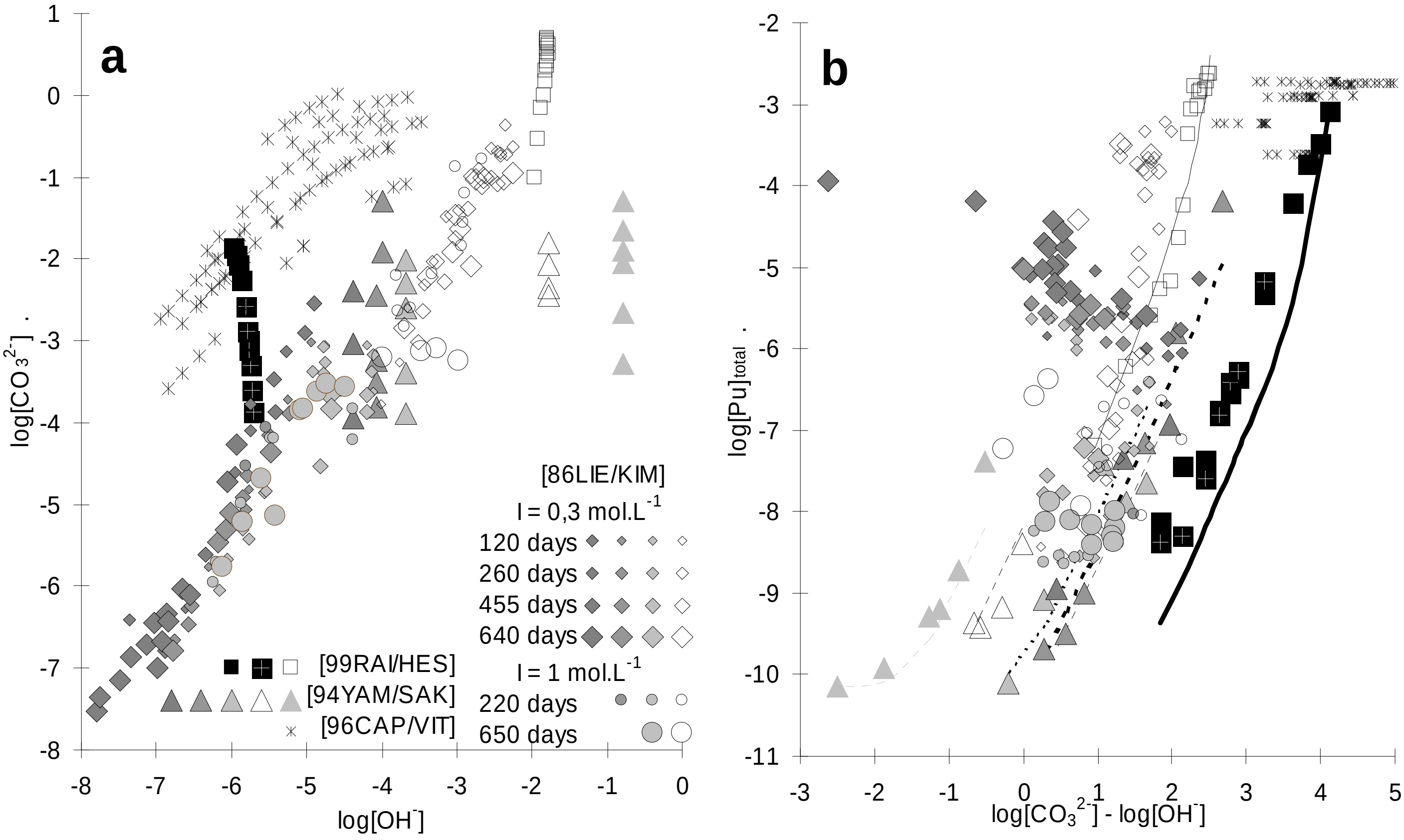

Fig.2: Pu(IV) experimental studies in $CO_3^{2-}/HCO_3^-/OH^-$ aqueous solutions: *in* **Fig.2a**, the **aqueous speciation** *for experimental studies of Pu(IV) is reported. [86LIE/KIM] (in $NaClO_4$), [94YAM/SAK] (in 0.1M KNO_3), [96CAP/VIT] (a spectrophotometric study during the titration ($2Na^+ + CO_3^{2-} + H_2O + CO_2(g) \rightarrow 2(Na^+ + HCO_3^-)$) and [99RAI/HES] (in $KHCO_3$ and 0.01MKOH + K_2CO_3) are Ref.[18], [9], [12] and [10], respectively. White symbols are for high values of Ratio [CO_3^{2-}]/[HCO_3^-]; the darkest grey are the symbols as this ratio decreases. In* **Fig.2b, experimental measurements of Pu(IV) solubility** *are plotted. The higher is the value of the [CO_3^{2-}]/[HCO_3^-]; ratio, the thicker are the lines. Continuous and dotted lines are calculated solubilities for the aqueous speciation of the studies from Ref.[9] and [10], respectively. The basic model to calculate the solubility (Eq.9) included species: PuO_2(am,hyd), $Pu(OH)_4$(aq), $Pu(CO_3)_4^{4-}$ and $Pu(CO_3)_5^{6-}$ [6]. To improve the fitting, several hypothetical species can be added to the basic model (see text and Tab.2). In Fig.2b we tentatively added the hypothetical species $Pu(CO_3)_2(OH)_3^{3-}$. For the data of Ref.[9 and 18], the values of logK_{s0} were assumed to be 0.8 and 2.1, respectively higher than for the data from Ref.[10]; this could as well reflect differences in pH calibration.*

actual M(IV) solubility as discussed just below. However, $M(CO_3)_2(OH)_2^{2-}$ can as well be used instead of $M(CO_3)_4^{4-}$ [10, 11]. We even tested other stoichiometries (Tab.2), but this sensitivity analysis exercise was not conclusive, as typically shown by the scattering of the data in Fig.2b. For this graphical representation, we took advantage, that at constant I experimental solubilities are expected to be on a single curve plotted as a function of (log[CO_3^{2-}]-log[OH^-]) (or log[HCO_3^-]), when the major aqueous complexes are of stoichiometries $Pu(CO_3)_3OH^{3-}$, $PuCO_3(OH)_3^-$, $Pu(CO_3)_2(OH)_2^{2-}$, $Pu(CO_3)_4^{4-}$ or $Pu(OH)_4$(aq) (Eq.9). Fortunately these 3 last stoichiometries are those under debate, while the limiting carbonate complex $Pu(CO_3)_5^{6-}$, predominates only at very high I and [CO_3^{2-}]. No thermodynamic interpretation (as typically difference in [CO_3^{2-}] or [OH^-], I influence or $Pu(CO_3)_5^{6-}$ formation) is enough to account for the scattering of the data (Fig.2b). For this reason, problems in the experimental measurements (or at least some of them) cannot be ruled out.

Beside possible unwanted oxidation in these measurements as already pointed out [10], irreversible formation of Pu(IV) polymer is ubiquitous. One must even avoid local conditions due to typically OH^- or pure water additions, where the polymer is (irreversibly) formed. We avoided this, by starting with the limiting carbonate complex, which prevents direct H_2O coordination on Pu^{4+} [12]. Polymer formation is a possible explanation for the scattering of solubility data from Ref.[8 and 18]. It could as well have been present in the work reported in Ref.[9], and even in the results in K_2CO_3 + 0.01 mol.L^{-1} KOH solutions reported in Ref.[10]. Successive filtrations or centrifugations can detect polymers, when they form solid particles (gel, colloids); unfortunately it can very well be soluble. For this reason, we only determined maximum possible values (Tab.2); but this does not allow determining stoichiometries of soluble polynuclear complexes. For keeping consistency with spectrophotometric studies, we used our [12] validated [6] value of k_5^0, the constant of $Pu(CO_3)_5^{6-}/Pu(CO_3)_4^{4-}$ Equilibrium, and obtained the formation constants of $Pu(CO_3)_5^{6-}$ and $Pu(CO_3)_4^{4-}$ by fitting experimental solubilities (Tab.2, Abstract). For improving the fit, we tentatively added $Pu(CO_3)_2(OH)_3^{3-}$ to the basic model (Fig.2b), in an attempt to keep consistency with the four sets of data [9, 10, 12 and 18]. However, experimental problems can very well explain the observed increase in solubility as compared to the solubility predicted with the basic model (*i.e.*. without any mixed soluble complex). For this reason the basic model can very well be sufficient, or other species should be added as typically $Pu(CO_3)_2OH^-$, $Pu(CO_3)_2(OH)_2^{2-}$, or $Pu(CO_3)_3^{2-}$ according to the results of our sensivity analysis (Tab.2).

Solubilities of actinides(IV), and the corresponding equilibrium constants compare well [6, 10]. There is no clear evidence of strong differences between actinides(IV) behaviours, even if uncertainties still exist on the stoichiometries of their complexes in $CO_3^{2-}/HCO_3^-/OH^-$ media; however in a quite narrow domain of chemical conditions. The experimental problems discussed for Pu certainly exist for other actinides (possibly to a lesser extend). It is not reliable to extract stoichiometries and corresponding formation constants of complexes from a limited set of measurements. We treated all the available experimental information (this will be published later for analogue actinides), in the same way as $M(CO_3)_2(OH)_2^{2-}$ was used to fit solubility data of several actinides M [10, 11].

Possible formation of Solid Solution (SoS) $Na_{2x-1}NpO_2(CO_3)_x(s)$ was already proposed and discussed [6, 15]. When two stoichiometric compounds are simultaneously stable, $[CO_3^{2-}]$ is buffered at $\log[CO_3^{2-}]_{1/2}$= -2.40 in 3M Na^+ media (Eq.25); while $\log[CO_3^{2-}]$ varies in a narrow domain, when the SoS is formed: $\log[CO_3^{2-}]= -2.40\pm^{+0.23}_{-0.12}$. The theoretical stability of the ideal SoS seems to be a broad domain, when plotted as a function of the stoichiometric coefficient x (thick grey lines are for $2 > x \geq 1$, Fig.3.a and b). However, this only corresponds to $\log[CO_3^{2-}]= -2.40\pm^{+0.23}_{-0.12}$ (Fig.1). The log/log plot best represents the experimental results because uncertainty is roughly the same for each point, and validating the using of MAL rather requires such log/log representations.

Non stoichiometric compounds (typically stoichiometric coefficient x = 0.8) were tentatively proposed to interpret X-ray diffraction patterns. However, when the compounds are equilibrated with aqueous solutions: x = 1 or 2 (for this reason, we chose these stoichiometries for the end-members of the hypothetical SoS). This was typically deduced from slope analysis of series of dissolutions / precipitations: x = 0.53, 0.89±0.06, 0.98±0.09, 0.94±0.07 and 0.95±0.09, and corresponding $\log K_{sx}$ = -8.18, -10.43±0.46, -11.33±0.59, -11.10±0.51 and -11.22±0.65, respectively, were fitted from the experimental results of Fig.1. Actually X-ray diffraction studies suggest a SoS of structure similar to those of compounds of x = 1 (rather than of x = 2): another end-member compound can be chosen, typically with $1 > x \geq 0.5$ ($x < 0.5$ is not possible for electroneutrality, while $x \rightarrow \infty$ (*i.e.* y = 0) corresponds to stoichiometry Na_2CO_3). However, no compound of stoichiometry $(NpO_2)_2CO_3(s)$ (*i.e.* x = 0.5) has been evidenced. Experimental solubilities at higher temperature could also suggest SoS for $0.5 < x < 2$. However, kinetics could as well interpret the shape of the solubility curves [23].

Furthermore, a dramatic effect on Np(V) solubility is only expected for small values of y (high values of x): NpO_2^+ would be at trace concentration in a matrix of stoichiometry Na_2CO_3, not treated here, since there is no evidence of such matrix incorporating Np. However, other matrix can be inferred (this is outside the scope of the present paper). Coprecipitation of trace elements is well documented, and indeed often treated (as Ionic Exchange) with Eq.22, while Eq.21 becomes equivalent to MAL for the end-member compound of the major element. The upper limit $\log[CO_3^{2-}]$ = -2.28 corresponds to x = 2, when $\log[CO_3^{2-}]$ is higher, x is also higher, and a dramatic decrease of Np(V) solubility is indeed predicted at $\log[CO_3^{2-}]$ = -2.0 (grey dashed line on Fig.1), if the SoS were stable: this is not observed experimentally. As a conclusion, only a SoS of stoichiometry x < 2 might be formed. For $2 > x \geq 1$ its effect on solubility would certainly be less than uncertainty. It might be metastable for $1 > x > 0.5$, while for dramatic lowering of Np(V) solubility (as expected for applications) it is needed to evidence a matrix, that would incorporate Np at trace concentrations.

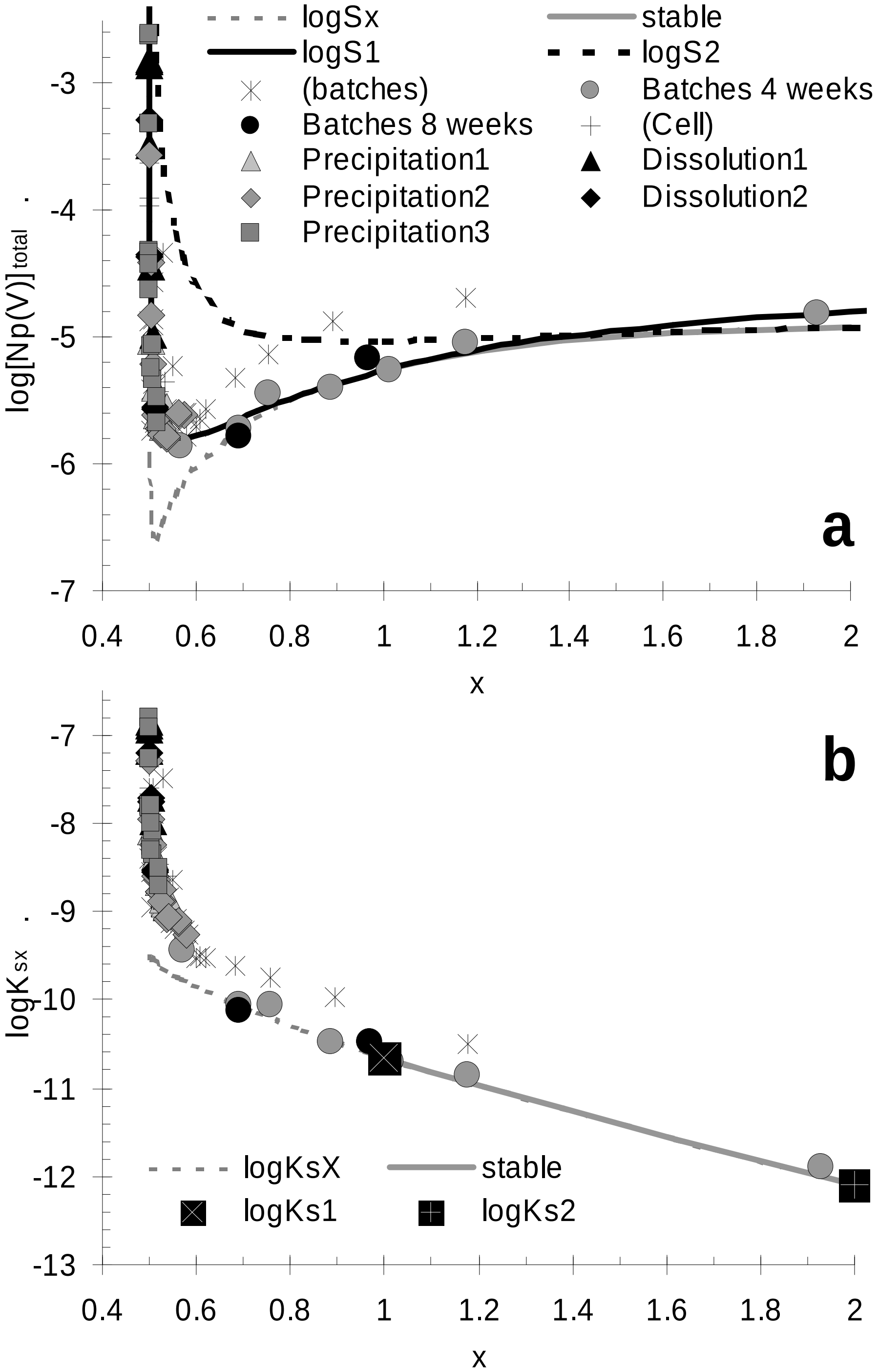

Fig.3: Possible stability of the $Na_{2x-1}NpO_2(CO_3)_x$ ideal solid solution: *$[NpO_2^+]$ was calculated (Eq.4) from $[Np(V)]_{total}$ (the experimental Np(V) solubilities (Fig.1 and 3.a)), and the experimental values of $[CO_3^{2-}]$ and $[Na^+]$. x (Eq.22) and K_{sx} (Eq.21, Fig.3.b) were calculated assuming the compounds of stoichiometries $NaNpO_2CO_3$ and $Na_3NpO_2(CO_3)_2$ in Fig.1 are the end-members of the solid solution. Legends are similar in Fig.1, 3.a and 3.b. S_x (Fig.3.a) is the solubility and K_{sx} (Fig.3.b) the product as defined in Eq.21 for the solid of stoichiometry $Na_{2x-1}NpO_2(CO_3)_x$.*

Eq.2 can be obtained from Eq.1 by deriving its stoichiometric coefficients. Conversely, this suggests "integrating" any ionic exchange equilibrium, interpreted as building the ionic exchange sites, *i.e.* the matrix (supporting them) as characterised by the two end-member compounds of the SoS. The ratio of their solubility products is fixed by the constant of the ionic exchange equilibrium. Integrating (MAL for this ionic exchange equilibrium) introduces another constant, which is enough to obtain both equilibrium constants (*i.e.* solubility products of both end-member compounds). For sorption end-members are rather surface compounds, the ratio of their solubility products can be measured as the equilibrium constant of ionic exchange equilibrium. However, interpreting dissolution / precipitation with equilibria similar to Eq.1 (and corresponding Eq.21) might very well be complicated by the formation of multilayer stoichiometric compounds, and by kinetics.

Before building TDB's for new systems, their correct thermodynamic description is needed. MAL for ideal systems is classically validated in the field of Solution Chemistry (*i.e.* systems are recognised or not to be ideal) by using log/log plots, where slopes are interpreted as (integer) stoichiometric coefficients. The same is not always tested for other systems, where MAL is used (or semi-empirical formula inferred from it). Determining the number of independent reactions is also a key parameter for using MAL: number of sites for typically sorption, ionic exchange [24] or ion binding by natural organic matters.

Acknowledgements

Christian Dautel measured Np(V) solubility. Diego Ferri and Ingmar Grenthe proposed an experimental methodology. Jean Massé sampled Np(V) compounds, and registered their X-ray diffraction patterns. Marie-Hélène Fauré reviewed geological literature on coprecipitation and SoS. She tested different models proposed in literature, and tested a former equivalent determination of the thermodynamic description presented in this paper, based on minimisation of solubility as a function of stoichiometric coefficient x. Serge Maillard gave the key idea: Eq.17 [7, 20]. He with Patrick Lovera checked mathematical developments. Pr.Gil Michard helped understanding the meaning of equations on SoS. Malcolm Rand gave useful comments on thermodynamic

data for UO_{2+x}.

References

[1] Muller, A., Radioact. Waste Manage. Nucl. Fuel Cycle, 6(2) (1985) 131-141

[2] (a) Grenthe, I., Fuger, J., Konings, R., Lemire, R., Muller, A., Nguyen-Trung, C., Wanner, H., *Chemical Thermodynamics of Uranium*. Elsevier (1992). (b) Grenthe, I., *personal communication*.

[3] Silva, R., Bidoglio, G., Rand, M., Robouch, P., Wanner, H., Puigdomenech, I., *Chemical Thermodynamics of Americium*. (1995)

[4] Grenthe, I., Puigdomenech, I., Sandino, A., Rand, M., *Appendix D* of Ref.[3] p.347-374

[5] Rard, J., Rand, M., Anderegg, G., Wanner, H., *Chemical Thermodynamics of Technetium* Elsevier (1999)

[6] Lemire, R., Fuger, J., Nitsche, H., Potter, P., Rand, M., Rydberg, J., Spahiu, K., Sullivan, J., Ullman, W., Vitorge, P., Wanner, H., *Chemical Thermodynamics of Neptunium and Plutonium*. Elsevier (2001)

[7] Vitorge, P., Capdevila, H., Maillard, S., Fauré, M.-F., Vercouter, T., Actinides 2001 Conf., J. Nuclear Sc. Techno. supplement 3, p.713-716 (2002)

[8] Kim, J., Lierse, C., Baumgartner F., ACS Symp. 216 (1983) 318

[9] Yamaguchi, T., Sakamote, Y., Ohnuki, T., Radiochim. Acta 66/67 (1994) 9-14

[10] Rai, D., Hess, N., Felmy, A., Moore, D., Yui, M., Vitorge, P., Radiochim. Acta 86 1-2 (1999) 89-99

[11] (a) Rai, D., Hess, N., Felmy, A., Moore, D., Yui, M., Radiochim. Acta 84 (1999) 159-170. (b) Rai, D., Felmy, A., Moore, D., Masson, A., MRS Symposium 353 (1995) 1143. (c) Rai, D., Felmy, A., Hess, N., Moore, D., J. Solution Chem. 26 (1997) 233-248. (d) Felmy, A., Rai, D., Sterner, S., Mason, M., Hess, N., Conradson, S., J. Solution Chem. 26 (1997) 233-248

[12] Capdevila, H., Giffaut, E., Vitorge, P., Delmau, L., Radiochim. Acta 74 (1996) 93-98

[13] Vitorge, P., Beaucaire, C., Fauré, M.-H., Maillard, S., Capdevila, H., *Solubilities of actinides in complex solutions. What are the solubility controlling phases in complex media?* Workshop on Solubility of Actinides in Relation with Nuclear Waste Matrices. Proceedings SCK.CEN, BLG 810 Mol (Belgium) 19-20/05/1999

[14] (a) Michard, G., *Equilibres chimiques dans les eaux naturelles* Publisud 1989. New edition: *Chimie des eaux naturelles* Publisud 2002. (b) Michard, G., *personal communication*.

[15] (a) Vitorge, P., Capdevila, H., CEA-R-5793 (1998). (b) Vitorge, P., IAEA-SR-104/25. Sofia Bulogaria (1984); (c) EUR 9543 (1985); (d) EUR 10023 (1985); (e) Grenthe, I., Riglet, Ch., Vitorge, P., Inorg. Chem. 25 (1986) 1679-84. (f) Riglet, Ch., Thesis Université Paris-6 (France 1989) and CEA-R-5535 (1990)

[16] Simakin, G., Sov. Radiochem. 19 (1977) 424-426

[17] (a) Kim, J., Klenze, R., Neck, V., Sekine, T., Kanellakopulos, B., RCM 01091, (1991). (b) Neck, V., Runde, W., Kim, J., Kanellakopulos, B., Radiochim. Acta 65 (1994) 29-37; (c) Neck, V., Runde, W., Kim, J., Kanellakopulos, B., Radiochim. Acta 65 (1994) 29-37; (d) Neck, V., Fanghänel, Th., Rudolph, G., Kim, J., Radiochim. Acta 69 (1995) 39-47 (e) Fanghänel, Th., Neck, V., Kim, J., Radiochim. Acta 69 (1995) 169-176; (f) Runde, W., Neu, M., Clark, D., Geochim. Cosmochhim. Acta, 60 (1996) 2065-2073

[18] Lierse, C., Kim, J., RCM 02286 (1986)

[19] Giffaut, E., Vitorge, P., Capdevila, H., CEA-N-2737 (1993) 22-29

[20] Maillard, S. *personal communication*.

[21] Guggennheim, E., *Mixtures* (Oxford 1952)

[22] Capdevila, H., Vitorge, P., Radiochim. Acta 82 (1998) 69-76

[23] Lemire, R., Boyer, G., Campbell, A., Radiochim. Acta 61 (1993) 57-63

[24] (a) Hiemstra, T., Van Riemsdijk, W., Bolt, G., Colloid Interface Sci. 133 (1989) 91. (b) Hiemstra, T., de Wit, J., Van Riemsdijk, W., ibid p.105. (c) Ly, J., Gorgeon, L., Le Vot, J.-C., Migration'93 Conf. (Charleston USA 1993) PC3-6 (d) Gorgeon, L., Thesis Université Paris 6 (France 1994)

[25] Vitorge, P., *Chimie des actinides.* Techniques de l'ingénieur BN 3520 (1999)

[26] Bourges, J., Guillaume, B., Koehly, G., Hobart, D., Peterson, J., Inorg. Chem. 22 (1983) 1179-1184

[27] Robouch, P., Thesis Université Louis Pasteur, Strasbourg (France 1987) and CEA-R-5473 (1989)

[28] Katz, J., Seaborg, G., Morss, L., *The chemistry of the Actinide Elements*. Vols.2 Chapman and Hall (1986)

[29] Musikas, C., Couffin, F., Marteau, M., J.Phys. et Chem. Phys. Biol. 71, 5 (1974) 641-648

[30] Krot, N., Gel'man, A., Mefod'eva, M., Shilov, V., Peretrukhin, V., Spitsyn, V., UCRL-Trans-11798 LLNL (1977)

[31] Peretruskhin, V., Shilov, V., Pikaev, A., WHC-EP-0817 (1995)

[32] Zielen, V., Cohen, D., J.Phys.Chem. 74 (1970) 394-405

[33] Shilov, V., Krot, N., Gel'man, A., Radiokhimiya 12 (1970) 697-699

[34] Peretrukhin, V., Krot, N., Gelman, A., Radiokhimiya 14 (1972) 72-77

[35] Nikolayevsky, V., Shilov, V., Krot, N., Radiokhimiya 16 (1974) 122-123

[36] Capdevila, H., Thesis Université Paris 11 Orsay (France 1992) and CEA-R-5643 (1993)

[37] Capdevila, H., Vitorge, P., Giffaut, E., Radiochim. Acta 58/59 (1992) 105-107

[38] Cassol, A., Magon, L., Tomat, G., Portanova, R., Inorg. Chem. 11 (1972) 515-519
[39] Vitorge, P., Tran The, P., EUR 13664
[40] Rai, D., Radiochim. Acta 35 (1984) 97-106

Tab.1: Solubility products, hydrolysis constants and standard potentials

The numerical values (at 25°C in standard conditions: aqueous solutions at I = 0) were estimated as indicated in footnotes (see also Ref.[25]), where alternative values are also indicated. The primary values (from which other values were calculated) are bolded. To stress indications of footnotes, values estimated by analogy are italicised[a], and a question mark[b] is added after species (first column) of unknown stoichiometry or possibly unstable. All ions are hydrated ions despite notation (aq) is omitted for simplicity. e^- is the notation of electrochemists (see text).

Standard redox potential (V/SHE)

	M =	U	Np	Pu	Am
$M^{3+} + 3e^- \leftrightharpoons M(s)$	$E^o_{3/0}$	-1.6_{46}[b,c]	-1.7_{72}[b,d]	-2.0_{00}[b,c]	-2.0_{68}[b,c]
$M^{3+} + e^- \leftrightharpoons M^{2+}$?	$E^o_{3/2}$				**$-2._3$**[b] ?
$M^{4+} + e^- \leftrightharpoons M^{3+}$	$E^o_{4/3}$	**-0.55_3**[b,e]	**0.21_9**[e]	**1.04_7**[e]	***$2._{487}$***[b,f,g]
$MO_2^+ + e^- + 4H^+ \leftrightharpoons M^{4+} + 2H_2O$	$E^o_{5/4}$	0.44_7[d]	**0.60_4**[b,e]	1.0_{33}[b,d]	0.481[b,d,g]
$MO_2^{2+} + e^- \leftrightharpoons MO_2^+$	$E^o_{6/5}$	**0.08_{78}**[e]	**1.15_9**[e]	**0.93_6**[e]	**1.5_{03}**[b,g,h]
[b]MO_3^+? $+ e^- + 2H^+ \leftrightharpoons MO_2^{2+} + H_2O$	$E^o_{7/6}$		**$2._{021}$**[i]	*$2._{285}$*[d,i]	*$2._{489}$*[d,i]
[b]$MO_2(OH)_6^{3-}$? $+ 2H^+ + e^- \leftrightharpoons 2H_2O + MO_2(OH)_4^{2-}$	$E^o_{VII/VI}$		**0.6_{32}**[b,j]	**0.8_{96}**[b,j]	**$1._{10}$**[b,j]
$M^{4+} + 4e^- \leftrightharpoons M(s)$	$E^o_{4/0}$	-1.3_{73}[b,d]	**-1.2_{74}**[b,c]	-1.2_{38}[b,d]	$-0._{929}$[b,d,g]
$MO_2^+ + 2e^- + 4H^+ \leftrightharpoons M^{3+} + 2H_2O$	$E^o_{5/3}$	-0.05_3[d]	0.41_1[b,d]	1.04_0[b,d]	***$1._{484}$***[b,g,k]
$MO_2^{2+} + 2e^- + 4H^+ \leftrightharpoons M^{4+} + 2H_2O$	$E^o_{6/4}$	**0.26_{73}**[e]	0.88_2[c,b]	0.98_4[b,d]	0.992[b,d,g]
$MO_2^{2+} + 3e^- + 4H^+ \leftrightharpoons M^{3+} + 2H_2O$	$E^o_{6/3}$	-0.00_6[d]	0.66_1[b,d]	**1.00_5**[b,e]	1.490[b,d,g]

Tab.1 *(continued)* **Standard equilibrium constants**

	M =	U	Np	Pu	Am
[b]$MO_2(OH)_6^{3-}$? $+ 4H^+ \leftrightharpoons$ [b]MO_3^+? $+ 5H_2O$	$-\log{}^*\beta^o_{VII,4}$		37.52[b,d]	*37.52*[a]	*37.52*[a]
$MO_2OH^+ + H^+ \leftrightharpoons MO_2^{2+} + H_2O$	$-\log{}^*\beta^o_{VI,1}$	**5.2**[e]	**5.1**[e]	**5.5**[e]	***5.5***[a]
$MO_2(OH)_2(aq) + 2H^+ \leftrightharpoons MO_2^{2+} + 2H_2O$	$-\log{}^*\beta^o_{VI,2}$	**10.3**[l]	***13.2***[a]	**$13._2$**[e]	***$13._2$***[a]
$MO_2(OH)_3^- + 3H^+ \leftrightharpoons MO_2^{2+} + 3H_2O$	$-\log{}^*\beta^o_{VI,3}$	**19.2**[e]	***19.2***[a]	***19.2***[a]	***19.2***[a]
$MO_2(OH)_4^{2-} + 4H^+ \leftrightharpoons MO_2^{2+} + 4H_2O$	$-\log{}^*\beta^o_{VI,4}$	**33**[e]	***33***[a]	***33***[a]	***33***[a]
$(MO_2)_2OH^{3+} + H^+ \leftrightharpoons 2MO_2^{2+} + H_2O$	$-\log{}^*\beta^o_{VI,2,1}$	**2.7**[b,e]			
$(MO_2)_2(OH)_2^{2+} + 2H^+ \leftrightharpoons 2MO_2^{2+} + 2H_2O$	$-\log{}^*\beta^o_{VI,2,2}$	**5.62**[e]	**6.27**[e]	**$7._5$**[e]	***$7._5$***[a]
$(MO_2)_3(OH)_4^{2+} + 4H^+ \leftrightharpoons 3MO_2^{2+} + 4H_2O$	$-\log{}^*\beta^o_{VI,3,4}$	**11.9**[b,e]			
$(MO_2)_3(OH)_5^+ + 5H^+ \leftrightharpoons 3MO_2^{2+} + 5H_2O$	$-\log{}^*\beta^o_{VI,3,5}$	**15.55**[e]	**17.1_2**[e]	**$2_{0.97}$**[b,m]	***$2_{0.97}$***[b,a]
$(MO_2)_3(OH)_7^- + 7H^+ \leftrightharpoons 3MO_2^{2+} + 7H_2O$	$-\log{}^*\beta^o_{VI,3,7}$	**31**[b,e]			
$(MO_2)_4(OH)_7^+ + 7H^+ \leftrightharpoons 4MO_2^{2+} + 7H_2O$	$-\log{}^*\beta^o_{VI,4,7}$	21.9[b,e]			
$MO_2OH(aq) + H^+ \leftrightharpoons MO_2^+ + H_2O$	$-\log{}^*\beta^o_{V,1}$	***11.3***[a]	**11.3**[e]	***11.3***[a]	***11.3***[a]
$MO_2(OH)_2^- + 2H^+ \leftrightharpoons MO_2^+ + 2H_2O$	$-\log{}^*\beta^o_{V,2}$	***23.6***[a]	**23.6**[e]	***23.6***[a]	***23.6***[a]
$MOH^{3+} + H^+ \leftrightharpoons M^{4+} + H_2O$	$-\log{}^*\beta^o_{IV,1}$	**0.54**[e]	**$0._{29}$**[e]	**0.7_8**[e]	***0.7_8***[a]
$M(OH)_4(aq) + 4H^+ \leftrightharpoons M^{4+} + 4H_2O$	$-\log{}^*\beta^o_{IV,4}$	*$7._5$*[a]	*$7._5$*[a,n]	$7._5$[d,o]	*$7._5$*[a]

$M_6(OH)_{15}^{9+} + 15H^+ \leftrightarrows 6M^{4+} + 15H_2O$	$-\log{}^*\beta^o_{IV,6,15}$	**16.9**[b,e]			
$MOH^{2+} + H^+ \leftrightarrows M^{3+} + H_2O$	$-\log{}^*\beta^o_{III,1}$	***6.8***[a]	**6.8**[e]	**6.9**[e]	**6.4**[e]
$M(OH)_2^+ + 2H^+ \leftrightarrows M^{3+} + 2H_2O$	$-\log{}^*\beta^o_{III,2}$	***14.1***[a]	***14.1***[a]	***14.1***[a]	**14.1**[e]
$M(OH)_3(aq) + 3H^+ \leftrightarrows M^{3+} + 3H_2O$	$-\log{}^*\beta^o_{III,3}$	***25.7***[a]	***25.7***[a]	***25.7***[a]	**25.7**[e]
$M(OH)_4^- + 4H^+ \leftrightarrows M^{3+} + 4H_2O$	$-\log{}^*\beta^o_{III,4}$	*$4_{0.05}$*[a]	*$4_{0.05}$*[a]	*$4_{0.05}$*[a]	$4_{0.05}$[d]
$M(OH)_4^- + H^+ \leftrightarrows M(OH)_3(aq) + H_2O$	$-\log{}^*K^o_{III,4}$	***$1_{4.35}$***[a]	***$1_{4.35}$***[a]	***$1_{4.35}$***[a]	**$1_{4.35}$**[p]
$MO_3.2H_2O(cr) + 2H^+ \leftrightarrows MO_2^{2+} + 3H_2O$	$\log{}^*K^o_{sVI,0}$	**4.81**[q]	**5.47**[e]	**$5._5$**[e]	***$5._5$***[a]
$M_3O_8(s) + 8H^+ \leftrightarrows M^{4+} + 2MO_2^{2+} + 4H_2O$	$3\lg{}^*K^o_{s2VI+IV,0}$	**2.46**[c]	***2.46***[a]	***2.46***[a]	***2.46***[a]
$M_3O_7(s) + 10H^+ \leftrightarrows 2M^{4+} + MO_2^{2+} + 5H_2O$	$3\lg{}^*K^o_{sVI+2IV,0}$	**-7.66**[c]	***-7.66***[a]	***-7.66***[a]	***-7.66***[a]
${}^sMO_2OH(s) + H^+ \leftrightarrows MO_2^+ + H_2O$	$\log{}^*K^o_{sV,0}$	***4.7***[a]	**4.7**[e]	**5.0**[e,r]	***4.7***[a]
$M_2O_5(s) + 2H^+ \leftrightarrows 2MO_2^+ + H_2O$	$2\lg{}^*K^o_{s2V,0}$	***3.70***[a]	**3.70**[c]	***3.70***[a]	***3.70***[a]
$M_4O_9(s) + 14H^+ \leftrightarrows 3M^{4+} + MO_2^{2+} + 7H_2O$	$4\lg{}^*K^o_{sVI+3IV,0}$	**-13.04**[c]	***-13.04***[a]	***-13.04***[a]	***-13.04***[a]
$M(OH)_4(s)^s + 4H^+ \leftrightarrows M^{4+} + 4H_2O$	$\log{}^*K^o_{sIV,0}$	***-2.0***[u]	***-2.0***[v]	**-2.0**[r,y]	***-2.0***[a]
${}^sM(OH)_4(s) \leftrightarrows M(OH)_4(aq)$	$\log{}^*K^o_{sIV,4}$	***-9.5***[a,y]	***-9.5***[a,y]	**-9.5**[r,y]	***-9.5***[a,y]
$MO_{1.61}(s) + 3.22H^+ \leftrightarrows 0.22M^{4+} + 0.78M^{3+} + 1.61H_2O$	$\log{}^*K^o_{s,0}$	***18.18***[a]	***18.18***[a]	**18.18**[c]	***18.18***[a]
${}^sM(OH)_3(s) + 3H^+ \leftrightarrows M^{3+} + 3H_2O$	$\log{}^*K^o_{sIII,0}$	*14.60*[a]	*14.60*[a]	*14.60*[a]	14.60[d]
${}^sM(OH)_3(s) \leftrightarrows M(OH)_3(aq)$	$\log{}^*K^o_{sIII,3}$	***-11.1***[a]	***-11.1***[a]	***-11.1***[a]	**-11.1**[w]
$M_3O_7(s) + 6H^+ \leftrightarrows M^{4+} + 2MO_2^+ + 3H_2O$	$3\lg{}^*K^o_{s2V+IV,0}$	-13.73[x]	*1.72*[a,x]	*-9.30*[a,x]	*9.61*[a,x]
$M_4O_9(s) + 10H^+ \leftrightarrows 2M^{4+} + 2MO_2^+ + 5H_2O$	$4\lg{}^*K^o_{s2V+2IV,0}$	-19.11[x]	*-3.66*[a,x]	*-14.67*[a,x]	*4.24*[a,x]

[a] Estimated by analogy (with a value in the same line)[b].

[b] Stoichiometry or numerical value needing experimental confirmation.

[c] Calculated from Gibbs energies of formation (Section Treatment of Data)[e,r].

[d] Calculated from other values in the same column.

[e] NEA-TDB reviews [2-6].

[f] We interpreted $E'^o_{IV/III}$, the formal potential of the $Am_{(IV)}/Am_{(III)}$ redox couple in Ref.[26, Fig.9] with Equilibrium $Am(CO_3)_5^{6-} + e^- \leftrightarrows Am(CO_3)_3^{3-} + 2\ CO_3^{2-}$ [27]. For correcting $E'^o_{IV/III}$ to standard conditions[z] we assumed $[CO_3^{2-}] + [HCO_3^-] = 2M$, despite the authors indicated, they prepared solutions by reacting $Na_2CO_3 + CO_2(g) + H_2O \rightarrow 2\ Na^+ + 2\ HCO_3^-$, rather corresponding to 2 M Na^+ media: $E^o_{IV/III} = 1.30_7 \pm 0.02_7$ V/SHE (1.96 σ hence not taking into account possible systematic errors on the calibration of the reference electrode, and on the chemical model). The smaller value $E^o_{IV/III} = 1.19 \pm 0.05$ was calculated possibly omitting molar to molal correction (formula for E'° p.277 in Ref.[3], however the main differences are in the ε values[z]. $E^o_{IV/III} = 1.30_7$ corresponds to $E'^o_{IV/III} = 0.94_5$V/SHE in 1 M CO_3^{2-} media, consistent with $0.92_4 \pm 0.01$ estimated by the authors. Assuming $\log(\beta_{5,Amp(IV)}/\beta_{3,Am(III)}) \approx \log(\beta_{5,Np(IV)}/\beta_{3,Np(III)}) = 1_{9.96}$ [6 p.267], corresponding to $1._{180}$V, $E^o_{4/3} = 2._{487}$V/SHE[g].

[g] $E^o_{4/3} = 2._{615}$, $E^o_{5/4} = 0._{838}$, $E^o_{6/5} = 1._{596}$, $E^o_{5/3} = 1._{727}$, $E^o_{6/4} = 1._{217}$, $E^o_{6/3} = 1._{683}$, $E^o_{3/0} = -2.0_{68}$, $E^o_{4/0} = -0._{897}$V/SHE[c].

[h] As for the $Am_{(IV)}/Am_{(III)}$ study[f], we interpreted $E'^o_{Am(VI/V)}$ [26, Fig.9], here with Equilibrium $AmO_2(CO_3)_3^{4-} + e^- \leftrightarrows AmO_2(CO_3)_3^{5-}$: $E^o_{Am(VI/V)} = 0.76_4 \pm 0.03_2$V/SHE (consistent with $0.77_5 \pm 0.03_8$ [3]) corresponding to $E'^o_{Am(VI/V)} = 0.96_9$V/SHE in 1 M CO_3^{2-} consistent with $0.97_5 \pm 0.01$ V/SHE estimated by the authors. The values of $\log(\beta_{3,M(VI)}/\beta_{3,M(V)}) = 14.19$, 13.87 and 13.0 for M = U, Np and Pu respectively (Ref.[6] p.267), correspond to 0.839, 0.820 and 0.769 V respectively. Linear extrapolation to Am gives $\log(\beta_{3,An(VI)}/\beta_{3,An(V)}) = 12.50$ corresponding to 0.7_{39} V, adding this to $E^o_{Am(VI/V)} = 0.76_4$, $E^o_{Am(6/5)} = 1.5_{03}$ V/SHE[g]. However, $E'^o_{Am(6/5)} =$

1.6 V/SHE in 1 M $HClO_4$ [28] is cited [3]; applying our I correction of 23 mV as for Np and Pu [6], $E^{o}_{Am(6/5)}$= 1.83 V/SHE.

[i] $E'^{o}_{7/6}$= 2.04, 2.3 and 2.5 V/SHE in 1 M $HClO_4$ for Np, Pu and Am, respectively, [29 and 30] cited in Ref.[31] p.2-4 and 2-5, for Np and Pu, respectively, and from Ref.[31] p.2-6. At I = 0 (pH = 0) An(VII) is destabilised by 19 mV[z]: $E^{o}_{7/6}$= 2.02_{1}, 2.2_{81} and 2.4_{81}V/SHE for An = Np, Pu and Am, respectively.

[j] The formal potential for Np, Pu and Am measured in 1M NaOH aqueous solution [31] are $E'^{o}_{VII/VI}$= 0.582 [32] or 0.587 V/SHE [33] (we used **0.585** V/SHE) for Np, **0.849** V/SHE for Pu [34] and **1.05** V/SHE for Am [35], we corrected these values to I = 0[z], and assumed they are $E^{o}_{VII/VI}$.

[k] Bourges et *al.* mixed $Am_{(III)}$ and $Am_{(VI)}$ in CO_3^{2-}/HCO_3^{-} media, and measured $[Am_{(III)}]$ during the reaction (Table II 24 in Ref.[26]). Two equilibria are needed to describe such systems [36, 37]. Using ($E'^{o}_{IV/III}$- $E'^{o}_{VI/V}$) measured by the same authors[f,h], and mass and electron balance equations we determined redox speciation, assuming equilibrium was achieved: $Am_{(IV)}$ and $Am_{(VI)}$ were always less than 1% of total Am, hence the reaction was $2\ AmO_2(CO_3)_3^{4-} + Am(CO_3)_3^{3-} + 2\ H_2O + 4\ CO_3^{2-} \leftrightharpoons 3\ AmO_2(CO_3)_3^{5-} + 4\ HCO_3^{-}$; we estimated the potential of the solution, and deduced $E'^{o}_{V/III}$= 0.8_{51}V/SHE assuming the medium was 1 M Na_2CO_3 + 1 M $NaHCO_3$ for equilibrium $AmO_2(CO_3)_3^{5-} + 4\ HCO_3^{-} + 2\ e^{-} \leftrightharpoons Am(CO_3)_3^{3-} + 2\ H_2O + 4\ CO_3^{2-}$. Extrapolation to I = 0 gives $E^{o}_{V/III}$= 0.8_{83}V/SHE[z]. Assuming $\log(\beta_{3,Am(V)}/\beta_{3,Am(III)}) \approx \log(\beta_{3,Np(V)}/\beta_{3,Np(III)}) = -3_{0.12}+1_{9.96} = 1_{0.16}$ (Ref.[6] p.267), corresponding to $0._{601}$V, $E^{o}_{5/3}$= $1._{484}$V/SHE[g].

[l] Maximum possible value[b,e].

[m] The same correction to I = 0 as for the corresponding Np value [6] was applied to the value measured at I = 1M [38].

[n] $-\log{}^{*}\beta^{o}_{Np(IV),4}$= 9.83 is calculated from Ref.[6] corresponding to $\log{}^{*}K^{o}_{sIV,4}$= -8.92.

[o] $-\log{}^{*}\beta^{o}_{Pu(IV),4}$= 6.93 (not 7.50) was tentatively discussed [6].

[p] Minimum possible value calculated from the maximum value $\log K_4$= -0.2 measured in concentrated KOH aqueous solution [39], extrapolated to I =0, assuming measurements in 1.58 M KOH: $\lg K^{o}_{III,4}$= -0.35, corresponding to $-\log{}^{*}K^{o}_{III,4}$= 14.35.

[q] Shoepite[c,s]

[r] Solubility calculated from this value needs experimental confirmation.

[s] Compounds written $A(OH)_z(s)$ (A = M or MO_2, and M = Np, Pu or Am) are often amorphous low temperature poorly characterised hydrated hydroxide or oxide compounds (typically MO_2(am,hyd) or microcrystalline MO_2) when experimental solubility are consistent with these tabulated data.

[t] We prefer here analogy, to avoid propagating possible inconsistency in further analogy for mixed valence compounds.

[u] $\log{}^{*}K^{o}_{sU(IV),0}$= -4.8 was estimated (but not selected) (Ref.[2] p.130, [4] p.349)[a,n,o,t,y]

[v] $\log{}^{*}K^{o}_{sNp(IV),0}$= 1.53 and $\log{}^{*}K^{o}_{sNp(IV),4}$= -8.3 were selected [6], however[a,t,y] it was discussed whether this might correspond to detection limit, and recent studies are indeed consistent with $\log{}^{*}K^{o}_{sNp(IV),4}$< -8.3.

[w] $\log{}^{*}K^{o}_{sAm(III),0}$= 17.0 and 15.2 were selected [3] for amorphous and crystalline compounds, respectively. We measured $\log{}^{*}K^{o}_{sAm(III),3}$= -11.1 [39].

[x] Calculated (but not used) as[d] $3\lg{}^{*}K^{o}_{s2V+IV,0}$= $3\lg{}^{*}K^{o}_{sVI+2IV,0}$ + $(E^{o}_{6/5}-E^{o}_{5/4})/0.05916$ and $4\lg{}^{*}K^{o}_{s2V+2IV,0}$= $4\lg{}^{*}K^{o}_{sVI+3IV,0}$+ $(E^{o}_{6/5}- E^{o}_{5/4})/0.05916$, when assuming $M_{(V)}$ and $M_{(IV)}$ (instead of $M_{(VI)}$ and $M_{(IV)}$) in solid compounds $M_3O_7(s)$ and $M_4O_9(s)$, the Np, Pu and Am values are set to the corresponding U values for ${}^{*}K^{o}_{s2V+IV,0}$ and ${}^{*}K^{o}_{sVI+2IV,0}$; in this case $3\lg{}^{*}K^{o}_{sVI+2IV,0}$= -23,11, -12,10 and -26,55 (instead of –7.66), and $4\lg{}^{*}K^{o}_{sVI+3IV,0}$= -28,48, -17,47 and -31,92 (instead of –13.04) for Np, Pu and Am, respectively.

[y] Assuming the thermodynamic stable phase should be MO_2(cr) rather than amorphous hydrated compound as tabulated here, it was pointed out $\log{}^{*}K^{o}_{sIV,4}$= -9.4 (or -13.4), -19.6 and –14.9 for U[u], Np[v] and Pu, while these

5-10 orders of magnitude difference is not reflected in actinide(IV) "solubility" measurements Ref.[6] p.324). $\log {}^*K^o_{sPu(IV),4} = -9.5$ is a maximum possible value, we typically used -10.14 (Tab.2, Fig.2b).

[z] The activity coefficients are calculated by using the SIT formula (Eq.12) and ε values [6], or estimating: $\varepsilon(Am(CO_3)_5^{6-},Na^+) \approx \varepsilon(Np(CO_3)_5^{6-},K^+) = -0.73$, $\varepsilon(AmO_2(CO_3)_3^{5-},Na^+) \approx \varepsilon(NpO_2(CO_3)_3^{5-},Na^+) = -0.53$, $\varepsilon(AmO_2(CO_3)_3^{4-},Na^+) = -0.15$, $\varepsilon(NpO_3^+,ClO_4^-) \approx \varepsilon(NpO_2^+,ClO_4^-) = 0.25$, $\varepsilon(MO_2(OH)_4^{2-},Na^+) = -0.15$, $\varepsilon(MO_2(OH)_6^{3-}, Na^+) = -0.2$

Tab.2 Equilibrium constants for Pu(IV) in CO_3^{2-}/HCO_3^- aqueous solutions

We estimated maximal possible values for $K^o_{si,j}$ (2nd column, Eq.10)[a] consistent with (only) the set of experimental solubilities published in Ref.[10], and deduced $\beta^o_{i,j}$ (3rd column)[b,c]. To cancel (or at least minimise) systematic deviations possibly originated in differences in the solid phases controlling solubilities in different studies, we also estimated $K^o_{si,j/4,0}$ (last column)[d] from experimental solubilities published in both Ref.[9 and 10]. However, this does not specially eliminate possible differences in pH calibration. I corrections were calculated (Eq.12) with published values for the ε coefficients [6], and $\varepsilon_{i,j}$ = 0.3, 0.2, -.05, -0.1, -0.15, -.7[a], -0.58[a] and -0.58 for aqueous species of charges +2, +1, -1, -2, -3, -4, -5 and -6, respectively.

$Pu(CO_3)_i(OH)_j^{(4-2i-j)+}$	$\lg K^o_{si,j}$ [e]	$\log\beta^o_{i,j}$ [e,b]	$\lg K^o_{si,j/4,0}$ [d,f]
Pu^{4+}	-58[c]	0	-37.0
$PuOH^{3+}$	-44.8	13.2	-23.8
$Pu(OH)_4(aq)$	<-10.1[g]	<47.9[g]	<-10.9[g]
$PuCO_3(OH)_3^-$	$<<-10._3$[h]	$<<47._7$[h]	<<5.4[h]
$Pu(CO_3)_2OH^-$	<-17.5[g]	<40.5[g]	<1.4[g]
$PuCO_3(OH)_4^{2-}$	$<<-6._2$[h]	$<<51._8$[h]	<<8.4[h]
$Pu(CO_3)_2(OH)_2^{2-}$	<-11.8[g]	<46.2[g]	<4.9[g]
$Pu(CO_3)_3^{2-}$	<-20.4[g]	<37.6[g]	<-1.1[g]
$Pu(CO_3)_2(OH)_3^{3-}$	<-7.5[g]	<50.5[g]	<8.9[g]
$Pu(CO_3)_3OH^{3-}$	<-16[g]	<42[g]	<2.9[g]
$Pu(CO_3)_3(OH)_2^{4-}$	<<-17[h]	<<41[h]	$<<4.0_1$[h]
$Pu(CO_3)_4^{4-}$	-21[a]	37	0
$Pu(CO_3)_3(OH)_3^{5-}$	$<<-17._5$[h]	$<<40._5$[h]	$<<3._{51}$[h]
$Pu(CO_3)_4OH^{5-}$	<<-19[h]	<<39[h]	<<2[h]
$Pu(CO_3)_3(OH)_4^{6-}$	$<<-19._5$[h]	$<<38._5$[h]	$<<1.5_1$[h]
$Pu(CO_3)_4(OH)_2^{6-}$	<<-21[h]	<<37[h]	<<0[h]
$Pu(CO_3)_5^{6-}$	-22.4[a]	35.6	-1.36[a]

[a] $\log k_{5,0} = \log(\beta_{5,0}/\beta_{4,0}) = \log(K_{s5,0}/K_{s4,0})$. $\lg k^o_{5,0}$=- 1.36 and $\Delta\varepsilon_{5,0}-\Delta\varepsilon_{4,0}$= 0.11 [12], where fixed, when $\lg K^o_{s4,0}$= -21 and $\varepsilon_{5,0}$ = -0.58 were fitted (Eq.9) on experimental solubilities in $KHCO_3$ and (K_2CO_3 + 0.01 M KOH) aqueous solutions respectively. This also generated $\lg K^o_{s5,0}$= -22.4 and $\varepsilon_{4,0}$= -0.7

[b] $K_{si,j} = K_{si0,0}\ \beta_{i,j}$

[c] $K_{s0,0}$ is the solubility product of PuO_2(am,hyd). $\log K_{s0,0}$ = -58 [6] (-57.4 [40] was used in Ref.[10])

[d] $K_{i,j/4,0} = K_{si,j}/K_{s4,0} = \beta_{i,j}/\beta_{4,0}$

[e] Estimated from the solubility data reported in Ref.[10]

[f] Estimated from the solubility data reported in both Ref.[9 and 10]

[g] Maximum possible value

[h] Adding this species does not improve the interpretation of available experimental information[g]