

Thermodynamic Stabilities of $\text{MO}_{2+x}(\text{s})$ (M = U, Np, Pu and Am), Pourbaix diagrams.

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The experimental solubilities of the hydrated amorphous freshly precipitated $\text{M}(\text{OH})_z(\text{am})$ and $\text{MO}_2(\text{OH})_z(\text{am})$ compounds are often used as an upper limit for the safety assessments of deep waste repositories, since these compounds slowly transform to less soluble ones, as typically $\text{M}(\text{OH})_4(\text{am})$ to $\text{MO}_2(\text{cr})$. Solubility (vs. redox potential) at $\text{pH}=8$, and E-pH predominance diagrams are plotted in aqueous solutions at 25°C by using thermodynamic data recently selected by the NEA-TDB review, or estimated by using classical chemical analogies for the non-redox reactions. The solubilities and relative stabilities are also calculated for the $\text{MO}_{2+x}(\text{s})$ crystalline compounds of known stabilities: $\text{U}_4\text{O}_9(\text{s})$, $\text{U}_3\text{O}_7(\text{s})$, $\text{U}_3\text{O}_8(\text{s})$ and $\text{Np}_2\text{O}_5(\text{s})$ where $2+x = 2.25, 2.33, 2.67$ and 2.5 respectively. The stabilities of the other $\text{MO}_{2+x}(\text{s})$ compounds are estimated by analogy: $\text{M}_4\text{O}_9(\text{s})$ (M=U, Np, Pu), $\text{M}_3\text{O}_7(\text{s})$ and $\text{M}_3\text{O}_8(\text{s})$ (M=U, Pu), and $\text{M}_2\text{O}_5(\text{s})$ (M=Np, Am) are predicted to be more stable (*i.e.* less soluble), than the amorphous hydroxides. However their precipitation have never been observed at room temperature possibly for kinetic reasons or difficulties in interpreting solubility experiments.

KEYWORDS: Uranium, Neptunium, Plutonium, Americium, thermodynamic, redox, hydrolysis, solubility

I. Introduction

In wet air conditions spent nuclear fuels are known to be oxidised to $\text{U}_4\text{O}_9(\text{s})$, $\text{U}_3\text{O}_7(\text{s})$ and eventually $\text{U}_3\text{O}_8(\text{s})$ ¹⁾, which might change physical properties of the matrix (spent fuel), that would possibly release some of its fission products as typically in possible interim storages. However this is not a problem for possible long term waste disposals, since safety assessment cannot rely on physical properties of the cladding and the matrix, while chemical properties of the disposal and the geological formation do not suffer this limitation: formation of new solid phases (including $\text{M}_4\text{O}_9(\text{s})$, $\text{M}_3\text{O}_7(\text{s})$ and $\text{M}_3\text{O}_8(\text{s})$) can only decrease the (equilibrium thermodynamic) solubility. For this reason, we calculated the solubilities of this type of compounds (see the abstract) by using the set of thermodynamic data recently validated by the NEA-TDB review (Thermodynamic Data Base project of the Nuclear Energy Agency OECD) for Uranium^{2),3)} Americium⁴⁾, and Neptunium and Plutonium⁵⁾ (we participated to this review).

II. Methodologies

1. Thermodynamic data

The thermodynamic data (noted with superscript^o when at 25°C , zero ionic strength: $I=0$) will be made available as supplementary materials^{6)*}. Only the most important additions and changes to the values recommended by the NEA-TDB review²⁾⁵⁾ are reported here. Ionic strength corrections were updated with recent ion pair parameters ϵ ⁵⁾.

Instead of $E^\circ_{6/5}=1.596$ and $E^\circ_{4/3}=2.615$ V/SHE as calculated from the values recommended by NEA-TDB⁴⁾ for the standard potential of the $\text{AmO}_2^{2+}/\text{AmO}_2^+$ and $\text{Am}^{4+}/\text{Am}^{3+}$ redox couples, we used the experimental measurements in

bicarbonate/carbonate media by Bourges *et al.*⁷⁾, and the shifts in potential from carbonate to acidic media (estimated as 0.739 V for the Am(VI)/Am(V) redox couple by analogy with other actinides⁵⁾, and using analogy with Neptunium⁵⁾ for the (IV)/(III) redox couples) for estimating: $E^\circ_{6/5}=1.503$ and $E^\circ_{4/3}=2.487$. Bourges *et al.*⁷⁾ also prepared Am(III), Am(IV), Am(V) and Am(VI) in bicarbonate / carbonate media, which we interpreted as previously for equilibria between four oxidation states of Plutonium⁸⁾⁹⁾. We interpreted with the reaction $2\text{AmO}_2(\text{CO}_3)_3^{4-} + \text{Am}(\text{CO}_3)_3^{3-} + 2\text{H}_2\text{O} + 4\text{CO}_3^{2-} \rightarrow 3\text{AmO}_2(\text{CO}_3)_3^{5-} + 4\text{HCO}_3^-$, where Am(VI) (and Am(IV)) had practically disappeared at equilibrium, and we estimated $E^\circ_{\text{V/III}}=0.851$ V/SHE for the Am(V)/Am(III) redox couple in $1\text{M Na}_2\text{CO}_3 + 1\text{M NaHCO}_3$ medium, and $E^\circ_{\text{V/III}} = 0.883$ at $I=0$, using again analogy with Np⁵⁾: $E^\circ_{5/3} = 1.484$ V/SHE for the $\text{AmO}_2^+/\text{Am}^{3+}$ redox couple, while $E^\circ_{5/3} = 1.727$ is calculated from the values recommended by NEA-TDB⁴⁾.

The values of $E_{7/6}$ and $E_{\text{VII/VI}}$, the formal potentials of the Np(VII)/Np(VI) redox couple in 1M HClO_4 and 1M NaOH respectively were taken from the review by Peretrukhin *et al.*¹⁰⁾, and extrapolated to $I=0$. The same potential shift between the two media was assumed for all the Actinides, and only the values¹⁰⁾ of the formal potentials of the M(VII)/M(VI) redox couples in 1M NaOH were considered (Pu(VII) and Am(VII) are less unstable in these media) resulting in $E^\circ_{\text{VII/VI}}=0.632, 0.896$ and 1.10 V/SHE, $E^\circ_{7/6}=2.02, 2.29$ and 2.49 V/SHE in acidic media for Np, Pu and Am respectively, and $\lg \beta^*_4=-37.52$ for Equilibrium $\text{MO}_3^{3+} + 5\text{H}_2\text{O} \Leftrightarrow \text{MO}_2(\text{OH})_6^{3-} + 4\text{H}^+$.

$\lg K^\circ_{\text{sIII},0}=17.0$ and 15.2 for Equilibrium $\text{Am}(\text{OH})_3(\text{s}) + 3\text{H}^+ \Leftrightarrow \text{Am}^{3+} + 3\text{H}_2\text{O}$ were selected by NEA⁴⁾ for amorphous and crystalline compounds. We choose a smaller value ($\lg K^\circ_{\text{sIII},0}=14.6$) based on our experimental minimum

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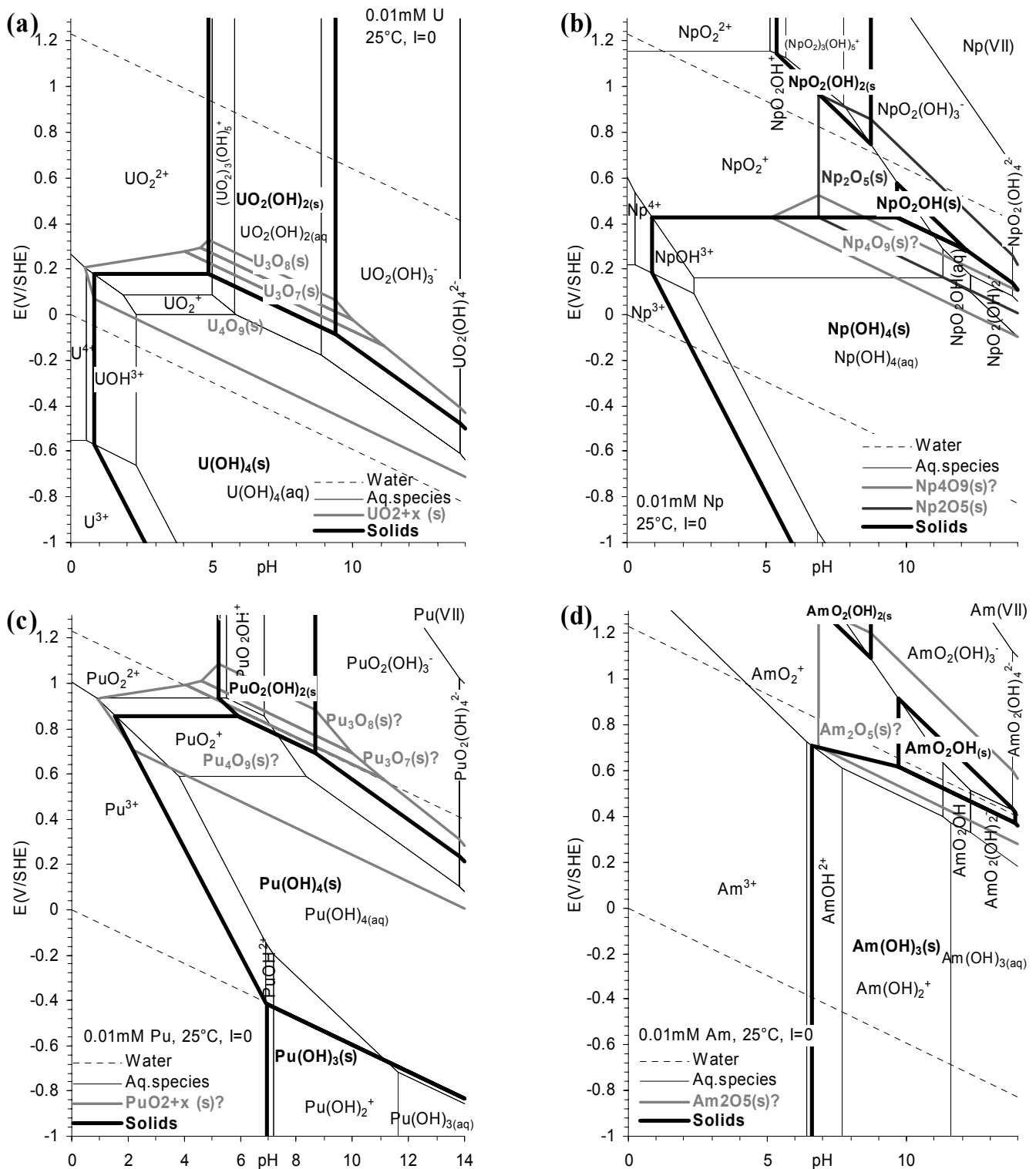


Fig.1 Pourbaix diagrams plotted with thermodynamic data selected by the NEA-TDB review⁽²⁻⁵⁾ or estimated by analogy (see text). The grey lines were added to the diagrams, they correspond to hypothetical control of the solubility by the corresponding compounds. At 25°C, $M(OH)_z(s)$ and $MO_2(OH)_z(s)$ compounds slowly transform to more stable $MO_{z/2}(s)$ (or $M_2O_z(s)$) not shown on this diagram (excepted $M_2O_5(s)$): this here increases the domain⁽²⁾ of $U_4O_9(s)$.

solubility⁽¹⁾: $\lg K_{sIII,3}^\circ = -11.1$ for Equilibrium $M(OH)_3(s) \leftrightarrow M(OH)_3$.

We calculated $\lg K_s^\circ = -13.04, -7.66$ and 2.46 for Equilibria

$$U_4O_9(s) + 14H^+ \rightarrow 3U^{4+} + UO_2^{2+} + 7H_2O \quad (1)$$

$$U_3O_7(s) + 10H^+ \rightarrow 2U^{4+} + UO_2^{2+} + 5H_2O \quad (2)$$

$U_3O_8(s) + 8H^+ \rightarrow U^{4+} + 2UO_2^{2+} + 4H_2O \quad (3)$ respectively, from standard Gibbs energies of formation for crystalline compounds⁽²⁾. Assuming the oxidation state of U is +4 and +6 in these MO_{2+x} compounds, Eq.(1-3) are non-redox reactions (see Abstract): we assumed K_s° 's for the

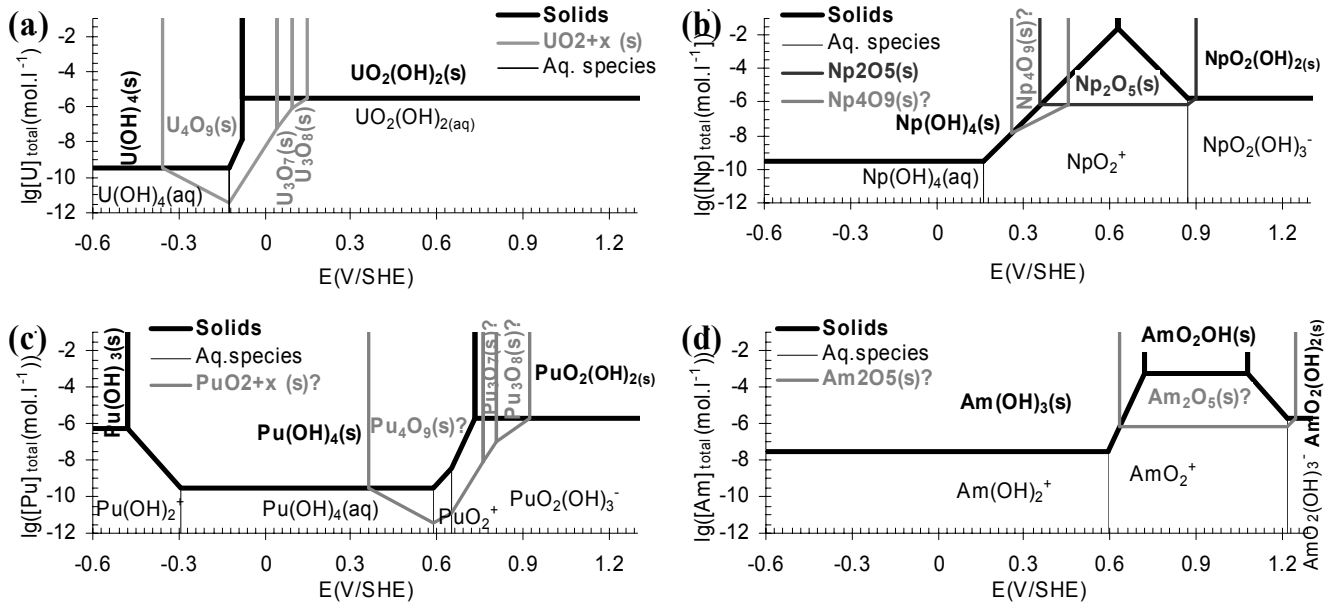
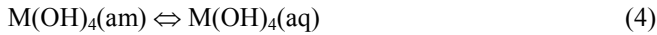


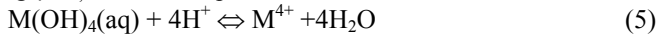
Fig.2 Solubility (lowest lines) diagrams at 25°C in aqueous solutions of pH=8 and I=0, plotted with the same data as Fig.1. other Actinides have the same values.

No solubility products based on solubility measurements for "amorphous" or "hydrated" UO_2 (or equivalently $\text{U}(\text{OH})_4$) could be selected by the NEA-TDB review^{2,3,5}: published determination for $\lg K_{s,0,\text{U(IV)}}^*$ ranged from 2.6 to 4.1, ($K_{s,0,\text{U(IV)}}^* = [\text{U}^{4+}]/[\text{H}^+]^4$); while for crystalline $\text{UO}_2(\text{cr})$ the value -4.8 was cited²). There are few experimental determinations for the Np compounds: $\lg K_{s,0,\text{Np(IV)}}^* = 1.5_3$ has been recommended⁵ for $\text{NpO}_2(\text{am,hyd})$, however -9.8 is calculated for crystalline $\text{NpO}_2(\text{cr})$ from recommended⁵ Gibbs energies of formation. Due to the disproportionation of Pu^{4+} in acidic aqueous media⁵⁽⁸⁾⁹, most of the published values for $\text{PuO}_2(\text{am,hyd})$ are questionable and we used $\lg K_{s,0,\text{Pu(IV)}}^* = -2.0$ as selected by the NEA⁵, consistent with our experimental determination¹²). This appears to be an upper value, for this reason (see Abstract) we also used this value for U, Np and Am.

Experimental solubilities of U^{2+} , Pu^{5+} and recently Np in near neutral aqueous solutions are $\lg K_{s,\text{IV,4}}^* \approx -9.5$; this might be an upper limit for the constant of Equilibria

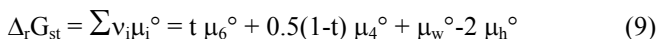
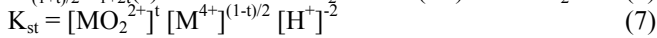
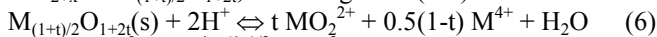


For this reason (see Abstract) we used this value resulting in $\lg \beta_{\text{IV,4}}^* \approx -7.5$ for Equilibria

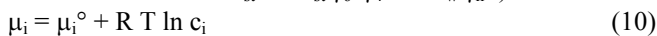


2. Solubility

Pourbaix and solubility diagrams are based on the well-established mass action law (see typically Eq.7). Writing MO_{2+x} as $\text{M}_{(1+t)/2}\text{O}_{1+2t}$, and using $t = x/(2-x)$:



where activity coefficients γ_i 's, are included in K_{st} (the standard constant is $K_{\text{st}}^\circ = K_{\text{st}} \gamma_6^t \gamma_4^{(1-t)/2} a_w \gamma_h^{-2}$)



is the chemical potential of the species MO_2^{2+} , M^{4+} , H_2O and H^+ for $i=6, 4, w$ and h respectively, and c_i the concentration. Equation(9) is obtained from the Gibbs-Duhem equation

$$0 = \left(\sum \mu_i v_i \right) d\xi \quad (11)$$

for fixed values of t . However $\text{MO}_{2+x}(\text{s})$ phases might very well be solid solutions: for that case we re-wrote Eq.(11) as

$$0 = \left(\sum \mu_i v_i \right) d\xi + \xi \left(\sum \mu_i (dv_i/dt) \right) dt \quad (12)$$

where the first term appears to be Eq.(9), and the chemical potentials for species in the solid phase are now

$$\mu_{s,i} = \mu_{s,i}^\circ + R T \ln \chi_i \quad (13)$$

where $\chi_{\text{MO}_2^{2+}} = t$, $\chi_{\text{M}^{4+}} = (1-t)/2$ and $\chi_{\text{O}^{2-}} = 1$. The standard states are identified by comparing¹³ Eq.(9) with

$$\Delta_r G_{\text{st}} = t \delta_6^\circ + 0.5(1-t) \delta_4^\circ + \mu_w^\circ - 2 \mu_h^\circ - \mu_{s,\text{O}^{2-}}^\circ \quad (14)$$

$$\Delta_r G_{\text{st}} = y \Delta_r G_b + (1-y) \Delta_r G_c \quad (15)$$

$$K_b^y K_c^{1-y} = [\text{MO}_2^{2+}]^t [\text{M}^{4+}]^{(1-t)/2} [\text{H}^+]^{-2} \quad (16)$$

where $\delta_i = \mu_i - \mu_{s,i}$, $t=b$ and c for the end members of the solid solution, $y = (t-c)/(b-c)$, and $K_{\text{sb}} = K_b^t ((1-t)/2)^{(1-t)/2}$ (the standard constant of Eq.6 is $K_b^\circ = K_b (\gamma_6/\gamma_{s,6})^t (\gamma_4/\gamma_{s,4})^{(1-t)/2} a_w$

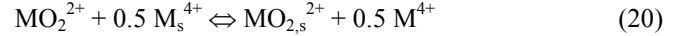
$\gamma_h^{-2} / \gamma_{s,\text{O}^{2-}}$). From $(\sum \mu_i (dv_i/dt))$ Eq.(12)

$$\Delta_r G_D = \delta_6^\circ - 0.5 \delta_4^\circ \quad (17)$$

$$D = (1-t)^{0.5} [\text{MO}_2^{2+}] / (2^{0.5} t [\text{M}^{4+}]^{0.5}) \quad (18)$$

$$D^{c-b} = K_c/K_b \quad (19)$$

corresponds to the ion exchange equilibrium



where i_s is the species i in the solid phase (the standard constant of Eq.20 is $D^\circ = D \gamma_6 \gamma_{s,4}^{0.5} / (\gamma_{s,6} \gamma_4^{0.5})$). Classically the ratio $[\text{MO}_2^{2+}]/[\text{M}^{4+}]$ is obtained from $E^\circ_{6/4}$ (as a function of the pH and the redox potential of the solution E), and substituted in Eq.(18): this gives t (vs. pH and E). Substituting t in Eq.(16) gives $[\text{M}^{4+}]$. From $E^\circ_{6/4}$, $E^\circ_{5/4}$ and $E^\circ_{4/3}$, $[\text{MO}_2^{2+}]$, $[\text{MO}_2^+]$ and $[\text{M}^{3+}]$ are calculated (vs. pH and E), from which the concentration of each complex is calculated (vs. pH and E) by using hydrolysis constants: the solubility is the sum of the concentrations for all these species.

Both equations (16) and (18) were given in literature¹³⁾, and should be used instead of the solubility product (Eq.(7)); but to our knowledge it was not clear they are simultaneously valid (Eq.12). The mathematical approach of Karpov *et al.* is certainly equivalent¹⁴⁾.

III. Results and discussions

Pourbaix (Fig.1) and solubility (Fig.2) diagrams were plotted (at I=0, 25°C, 1 atm) for the amorphous hydrated hydroxides or oxides¹⁵⁾, where M_2O_5 compounds, and then mixed valence compounds MO_{2+x} (written M_iO_j) were added. Stabilities and solubilities of possible solid solutions are not shown on the figures since they would not change the qualitative discussion in the present section. However retention of trace concentration for typically Np or Pu (in UO_2 or UO_{2+x} matrix) is expected through typically ionic exchange equilibria (Eq.18-20).

An oxidative perturbation would first result in the formation of U(VI), Np(V) or Pu(V) soluble species (Fig.1), while Am(V) is only formed in very aggressive conditions (as typically strong radiolysis in chloride media) that can oxidise water (Fig.1d).

As a consequence of the analogy used to estimate their stabilities, M_iO_j domains are very similar but shifted upward with decreasing stability of M(VI): $U(VI) > Np(VI) > Pu(VI) \gg Am(VI)$ (Fig.1). Pu_3O_8 would typically oxidise water (Fig.1c). Similarly the stability of freshly precipitated $M(OH)_4$ solids in contact with water, increases along the series $Pu(IV) > Np(IV) > U(IV) \gg Am(IV)$ (Fig.1, 2). These variations are complicated by M(V) possible stability which increases in the series $Np(V) > Pu(V) > Am(V) > U(V)$ (Fig.1). The high Np(V) stability induces relatively high Np solubility (Fig.2.b). To a lesser extent, Pu(V) can also contribute to Pu solubility (Fig.2c). Fig.2 confirm $M(OH)_4(s)$ solubility product is a key parameter for performance assessment of waste disposal in deep geological formation, where reducing conditions are expected.

Figure 2.a illustrates the decrease in Uranium solubility as a result of the formation of $U_4O_9(s)$, $U_3O_7(s)$ and $U_3O_8(s)$ crystalline compounds, when compared to the solubility of the freshly precipitated amorphous hydrated compound $U(OH)_4(am,hyd)$. Similar effect (not shown on the figure) is expected for more stable crystalline U(IV) compounds; but the domain of stability for $U_4O_9(s)$ would be much smaller²⁾ than the one shown in Fig.1.a-2.a. Similarly $Np_2O_5(s)$ decreases the (long term) solubility of Neptunium as compared to $NpO_2(am,hyd)$.

Several hypothetical phases are also predicted to lower such solubilities in non-reducing to oxidising conditions: $Np_4O_9(s)$, $Pu_4O_9(s)$, $Pu_3O_7(s)$ and $Pu_3O_8(s)$. However no experimental evidence of their formations was found by the NEA-TDB review²⁾⁵⁾. To our knowledge, there is even no clear experimental evidence, that Uranium solubility can be controlled by $U_4O_9(s)$, $U_3O_7(s)$ or $U_3O_8(s)$ compound at typically room temperature. This might very well be attributed to kinetic limitations. Our calculations at least

indicate the order of magnitude of the decrease in solubilities as expected by the formation of $MO_{2+x}(s)$ compounds.

Acknowledgment

This work received some financial support from ANDRA.

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