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**The possible effects of alfa and beta  
radiolysis on the matrix dissolution  
of spent nuclear fuel**

I Grenthe  
I Puigdomènech  
J Bruno

Department of Inorganic Chemistry  
Royal Institute of Technology  
Stockholm, Sweden January 1983

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*POSTADRESS: Box 5864, 102 48 Stockholm, Telefon 08-67 95 40*

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THE MATRIX DISSOLUTION OF SPENT NUCLEAR FUEL

I Grenthe  
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Matrix Dissolution of Spent Nuclear Fuel

I. Grenthe, I. Puigdomènech and J. Bruno

Department of Inorganic Chemistry, Royal Institute of  
Technology, Stockholm, Sweden

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### Summary

The effects of oxidants on the retainment of actinides in a nuclear repository have been modelled by using an equilibrium procedure. The oxidants are formed as a result of  $\alpha$ - and  $\beta$ -radiolysis when spent nuclear fuel is exposed to ground water. From an equilibrium point of view, the strongest reductants in the system (Zr, Pb and Cu) are expected to be oxidized first, leaving the actinoids in the oxidation states they have in the fuel matrix. This is expected to result in a negligible mobilization of the actinoids due to the very low solubility of the  $\text{MO}_2$  oxides. However, the formation of protective layers of oxides will most likely decrease the effectiveness of the metallic reducing agents. This will lead to an increased oxidation of the spent fuel which results in an increased actinoid mobilization.

The results of the equilibrium calculations show that the oxidation of the fuel matrix results in the formation of  $\text{UO}_2(\text{OH})_2(\text{s})$  and to the formation of the soluble complex  $\text{UO}_2(\text{CO}_3)_3^{4-}$ . The transport of uranium is limited by the total concentration of carbonate in the aqueous phase.

Neptunium may be quantitatively solubilized as various  $\text{Np}(\text{V})$  species and transported by ground water from the repository.

Plutonium is retained at the repository site as insoluble  $\text{PuO}_2$ . Only very small amounts are transported by ground water.

The mobile actinoids may be reprecipitated when they encounter reducing conditions along the flow path. The conditions for reprecipitation for typical ground water compositions have been modelled by using solubility - pe diagrams.

## INTRODUCTION

This Report is an attempt to evaluate the combined effects of  $\alpha$ - and  $\beta$ -radiolysis on the chemical stability of the  $UO_2$ -matrix of spent nuclear fuel.

It will be assumed that the nuclear waste matrix - uranium, neptunium and plutonium oxides - surrounded by zircalloy cladding, is contained in canisters made of copper and lead. If the metal canister is damaged by corrosion or mechanical failure in its geological environment, its contents will come into contact with ground water. The radioactive material may then be transformed and/or dissolved and ultimately transported to the biosphere.

The aim of this Report is to assess the effects of  $\alpha$ - and  $\beta$ -radiolysis on the dissolution of the spent fuel matrix by ground waters. A chemical equilibrium method will be used to model this process.

### Chemical Background

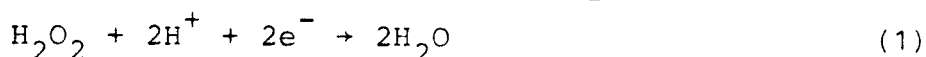
Interaction between ionizing radiation and water produces equivalent amounts of oxidizing and reducing species like free radicals, solvated electrons and molecules. The final reductant is usually chemically fairly inert  $H_2(g)$ , while the oxidant may be  $H_2O_2$  or  $O_2(g)$ . The rates and mecha-

nism of radiolysis in ground water systems have been discussed in detail by Christensen and Bjergbakke [1].  $\alpha$ - and  $\beta$ -radiolysis takes place when the ground water comes in contact with the spent nuclear fuel, after destruction of the outer metal canister.  $\alpha$ - and  $\beta$ -particles can only penetrate the water layer in the close vicinity of the nuclear waste, and surface effects on the rate of formation/recombination may therefore be important. The present state of knowledge does not permit effects of this type to be taken into account, when making the theoretical calculations.

The total production of hydrogen (and the equivalent amount of oxygen) is strongly dependent on the exposed fuel area and the concentration of dissolved species in the aqueous phase [1]. In order to model the effects of  $\alpha$ - and  $\beta$ -radiolysis, we have used the assumptions of Christensen and Bjergbakke. We will present results for two different cases, radiolysis in a system with an intact bentonite buffer [1, Tables 8 and 9], and radiolysis in pure water [1, Table 15]. The latter case represents a conservative approach, where the effects of radiolysis are expected to be much larger than in a ground water situation.

The effects of oxidants ( $\text{H}_2\text{O}_2$  or  $\text{O}_2$ ) on the fuel dissolution have been modelled by using an equilibrium approach. The calculations are not influenced by the mechanism of radiolysis. Only the total amounts of oxidants produced have been considered, i.e. the possible reducing effects of  $\text{H}_2$  have been neglected.

Initially, the chemical system contains actinide(IV) oxides and a fairly large amount of metallic material. The latter are all potential reducing agents. Hydrogen peroxide and oxygen which are strong oxidants are introduced into the systems through radiolysis. The  $H_2O_2$  will react according to



Oxidation of  $UO_2(s)$  will ultimately result in the formation of soluble uranium(VI) carbonato complexes. The formation of such species will lead to an increased rate of dissolution of the spent fuel matrix.

The type and amount of the various materials in nuclear waste canisters are given in Table 1.

Table 1. The material content of one nuclear waste copper canister

Component	Amount	
Cu(s)	$1.55 \cdot 10^4$ kg	$2.4 \cdot 10^5$ mol
$UO_2(s)$	$1.4 \cdot 10^3$ "	$5.2 \cdot 10^3$ "
$PuO_2(s)$	10 "	37 "
$NpO_2(s)$	5 "	19 "
Zr(s)	390 "	$4.3 \cdot 10^3$ "
Pb(s)	$2 \cdot 10^3$ "	$9.7 \cdot 10^3$ "

The following assumptions have been made

- chemical equilibrium is attained in the system
- the chemical species that may be formed and their equilibrium constants are those given in Appendix 1
- the effects of radiolysis on one fuel canister which is broken immediately after storage is considered



- the canister is exposed to a constant flow of one litre of ground water per year
- the time dependence of radiolysis is modelled by making model calculations over six different time intervals.

The composition of the system at the origin ( $t = 0$ ) is known. During a period of time,  $t$ , a volume of water equal to  $V_t$ , comes in contact with the canister.  $V_t$  is assumed to be known from the hydrology of the area and from the permeability of the surrounding rock matrix and back-fill materials (one litre per canister and year). The amount of oxidants in mol,  $n_{\text{OX}}^t$ , produced during the time interval  $t$  is taken from [1]. These data are given in Table 2.

Table 2. Flow volumes of ground water and the amounts of oxidant  $n_{\text{OX}}^t$  generated per canister during different time intervals

Year number	$V_t$ litres	Amount of oxidants, $n_{\text{OX}}^t$ , generated in the system during the time interval	
		Case I [1, Table 15]	Case II [1, Table 8, 9]
1	1	5	$1 \cdot 10^{-3}$
260	260	$0.86 \cdot 10^3$	0.200
960	700	$1.24 \cdot 10^3$	0.400
$9.96 \cdot 10^3$	$9 \cdot 10^3$	$6.50 \cdot 10^3$	3.24
$10^5$	$9 \cdot 10^4$	$12.0 \cdot 10^3$	19.16
$10^6$	$9 \cdot 10^5$	$8.4 \cdot 10^3$	120

Knowing the total amount of each chemical component in the closed system (canister and the amount of ground water in contact with it during the time interval) at a time  $t$ , one can calculate the equilibrium composition. During the time interval some chemical changes have occurred, new solid phases have been formed and some soluble species have been formed. These changes are taken into account when the model calculation is repeated for the next time interval, and so on. From these data one obtains the total amounts of material that has left the system as soluble species, the composition of the predominant soluble species and the amounts of solid material transformed.

### Calculations

The program SOLGASWATER [2] (in a modification written in this department) was used. The program calculates the activity and concentration of each species, using as input data,

for each component: -

the total amount (in mol) per litre of fluid phase present in the system.

for each complex (soluble or solid):

the equilibrium constant of formation,  
the stoichiometric coefficients.

For redox equilibria, one uses the well known relation:

$$\log \beta = n_e E^0 / g \quad (\text{where } g = \ln(10)RT/F = 0.059 \text{ V at } 25^\circ\text{C}).$$

In the same way, one can calculate the redox potential from the electron activity:  $E = -g \log\{e^-\} = g pe$ .

No corrections were made for changes in the equilibrium constants due to variations in the ionic media, i.e. the activity coefficients were kept equal to 1.

Equilibrium data were taken from the literature, they are summarized in Appendix 1.

Data for some equilibria were not available in the literature, this is the case for carbonate complexes of neptunium and plutonium in all oxidation states. In these cases, we used uranium(IV), (V) and (VI) data as models, while the Pu(III) data were modelled by using the corresponding lanthanides(III) equilibrium constants. In view of the chemical similarities between these systems, this procedure was considered satisfactory.

Both uranium and the other actinides may form peroxo complexes. The net effect of this might be to decrease the total concentration of oxidants in the system. A model calculation on uranium indicated that the concentration of peroxo complexes is negligible except at high pe (Fig. 1). Hence, the formation of peroxo complexes will not influence the solubility of the  $UO_2$  matrix under the conditions present in the nuclear repository.

Equilibrium constants for 87 soluble complexes and 23 solid phases were included in the calculations. All data refer to 298 K and 101 kPa (1 atm.). The ground water was assumed to contain a total carbonate concentration of  $2 \cdot 10^{-3}$  M ( $\sim 120$  ppm). In order to study how the system is influenced by this quantity, some calculations were repeated at a total carbonate concentration of  $4 \cdot 10^{-3}$  M and 0 M.

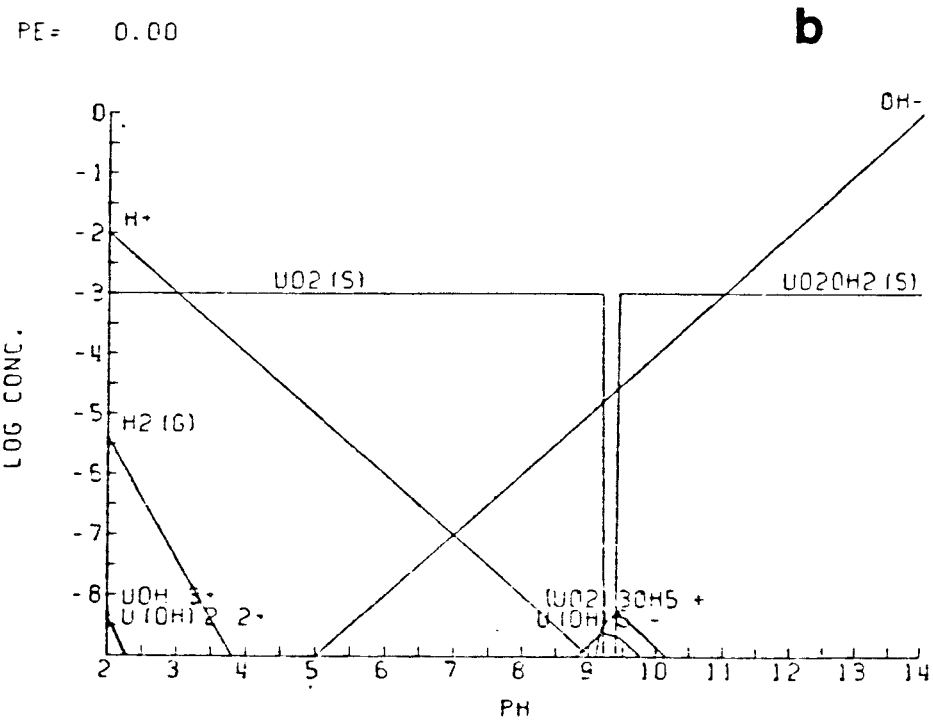
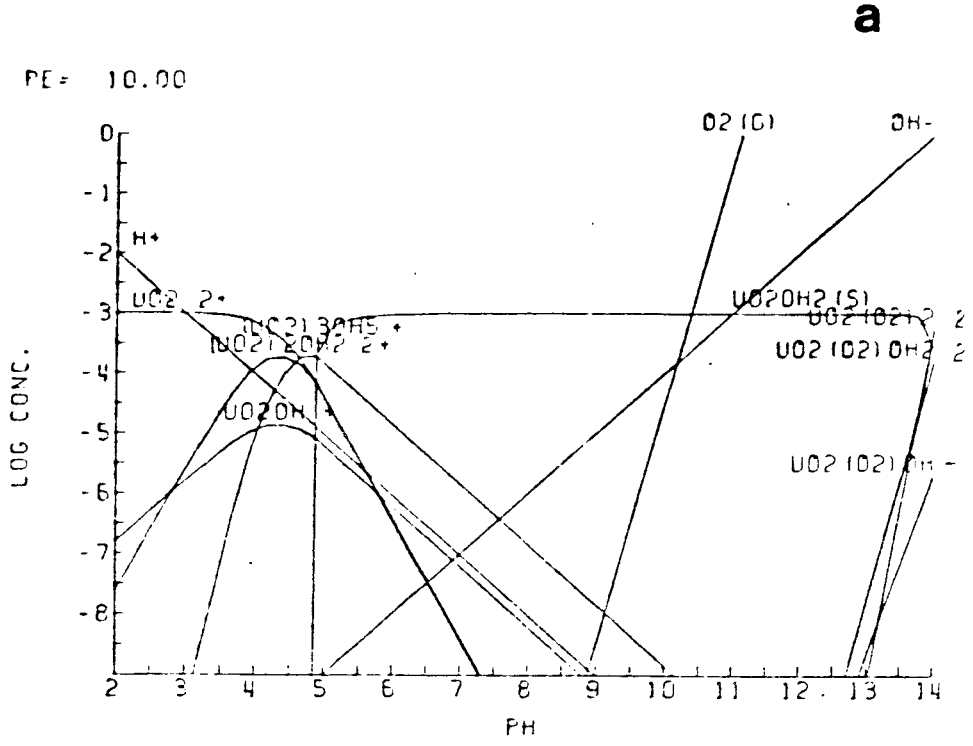
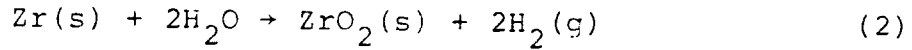


Figure 1. Logarithmic diagrams for the system: uranium,  $H^+$ ,  $e^-$ , at  $U_{Tot} = 1 \text{ mM}$ .  
 a:  $pe = 10$ ; b:  $pe = 0$ . The existence of peroxo complexes is shown at  $pH > 13$ ,  $pe = 10$ .

The calculations have been made using the time intervals given in Table 2. Zr(s) is not thermodynamically stable in water and forms H<sub>2</sub>(g) and ZrO<sub>2</sub>(s)



No credit has been given for the capacity of Zr(s) for reducing actinides. Reaction (2) is kinetically slow and it is therefore likely that Zr(s) will be present in the system for a long time, thus increasing the likelihood that it may act as a reductant for actinides.

In order to study the effects of the metal container on the solubilization of UO<sub>2</sub>(s) and other actinides, we performed a second set of equilibrium calculations, now without canister material in the system. By this procedure, we can model the effect of a coating of the metals with a protective layer of corrosion products.

## RESULTS AND DISCUSSION

The results of the model calculations for the system containing UO<sub>2</sub>(s) and canister are presented in Tables 3 and 4.

Table 3 presents the total amount of the solubilized components in mol as a function of time. The final values of pH and pe are also included.

Table 4 presents the main soluble species and solid phases in the same system.

Table 3. Results of the calculations for the system: matrix, metal canister and 2mM bicarbonate solution.

Number of Years	pH	pe	Amount solubilized (mol)					
			Cu	Zr	U	Np	Pu	Pb
Case I								
1	8.3	-11.0	$2 \cdot 10^{-20}$	$3 \cdot 10^{-10}$	$3 \cdot 10^{-10}$	$2 \cdot 10^{-12}$	$8 \cdot 10^{-11}$	$2 \cdot 10^{-17}$
260	11.3	-7.2	$3 \cdot 10^{-14}$	$6 \cdot 10^{-5}$	$8 \cdot 10^{-5}$	$5 \cdot 10^{-7}$	$2 \cdot 10^{-8}$	0.01
960	10.7	-6.7	$2 \cdot 10^{-13}$	$5 \cdot 10^{-5}$	$6 \cdot 10^{-5}$	$4 \cdot 10^{-7}$	$1 \cdot 10^{-8}$	0.02
9960	11.2	-7.2	$1 \cdot 10^{-12}$	$2 \cdot 10^{-3}$	$2 \cdot 10^{-3}$	$1 \cdot 10^{-5}$	$4 \cdot 10^{-7}$	0.44
$10^5$	11.2	-3.2	$2 \cdot 10^{-7}$	0.02	0.02	$1 \cdot 10^{-4}$	$4 \cdot 10^{-6}$	4.
$10^6$	11.2	-3.2	$2 \cdot 10^{-6}$	0.2	0.22	$1 \cdot 10^{-3}$	$4 \cdot 10^{-5}$	43.
Case II								
1	8.3	-11.0	$2 \cdot 10^{-20}$	$3 \cdot 10^{-10}$	$3 \cdot 10^{-10}$	$2 \cdot 10^{-12}$	$8 \cdot 10^{-11}$	$2 \cdot 10^{-17}$
260	9.9	-7.0	$4 \cdot 10^{-14}$	$2 \cdot 10^{-6}$	$3 \cdot 10^{-6}$	$2 \cdot 10^{-8}$	$6 \cdot 10^{-10}$	$4 \cdot 10^{-5}$
960	9.5	-6.8	$2 \cdot 10^{-13}$	$3 \cdot 10^{-6}$	$4 \cdot 10^{-6}$	$2 \cdot 10^{-8}$	$7 \cdot 10^{-10}$	$7 \cdot 10^{-5}$
9960	9.4	-6.8	$3 \cdot 10^{-12}$	$3 \cdot 10^{-5}$	$3 \cdot 10^{-5}$	$2 \cdot 10^{-7}$	$7 \cdot 10^{-9}$	$9 \cdot 10^{-4}$
$10^5$	9.1	-6.6	$4 \cdot 10^{-11}$	$1 \cdot 10^{-4}$	$2 \cdot 10^{-4}$	$1 \cdot 10^{-6}$	$4 \cdot 10^{-8}$	$9 \cdot 10^{-3}$
$10^6$	9.4	-6.8	$2 \cdot 10^{-10}$	$3 \cdot 10^{-3}$	$4 \cdot 10^{-3}$	$2 \cdot 10^{-5}$	$8 \cdot 10^{-7}$	0.09

Table 4. Main soluble species and solid phases for the system: matrix, metal canister and 2mM bicarbonate solution. Case I.

Component	Years:	
	960 (pH=10.7, pe=-6.7)	10 <sup>6</sup> (pH=11.2, pe=-3.2)
Cu	Cu <sup>+</sup> , Cu(s)	Cu <sup>+</sup> , Cu(OH) <sub>3</sub> <sup>-</sup> , Cu(s), Cu <sub>2</sub> O(s)
Zr	Zr(OH) <sub>5</sub> <sup>-</sup> , ZrO <sub>2</sub> (s)	Zr(OH) <sub>5</sub> <sup>-</sup> , ZrO <sub>2</sub> (s)
Pb	Pb(OH) <sub>2</sub> , Pb(OH) <sub>3</sub> <sup>-</sup> Pb(s), PbO(s)	Pb(OH) <sub>3</sub> <sup>-</sup> , PbO(s), Pb <sub>3</sub> (OH) <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub> (s)
U	U(OH) <sub>5</sub> <sup>-</sup> , UO <sub>2</sub> (s)	U(OH) <sub>5</sub> <sup>-</sup> , UO <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> <sup>4-</sup> , UO <sub>2</sub> (s)
Np	Np(OH) <sub>5</sub> <sup>-</sup> , NpO <sub>2</sub> (s)	Np(OH) <sub>5</sub> <sup>-</sup> , NpO <sub>2</sub> (s)
Pu	Pu(OH) <sub>5</sub> <sup>-</sup> , PuO <sub>2</sub> (s)	Pu(OH) <sub>5</sub> <sup>-</sup> , PuO <sub>2</sub> (s)

From the calculations, we can conclude that the solubilization of actinides in the waste material is negligible for both cases I and II, provided equilibrium is attained. The main reductant is Cu(s) which is transformed to Cu<sub>2</sub>O(s).

It is not probable that an equilibrium situation such as the one used to obtain the data in Tables 3 and 4 will be attained. It is more likely that Cu(s) will be "passivated" by the formation of oxide coatings. For this reason we have also investigated the effects of radiolysis in the absence of canister materials and cladding. The results are presented in Tables 5 and 6.

Table 5. Results of the calculations for the system: matrix and 2mM bicarbonate solution. The amounts of solubilized matrix in a calculation, were withdrawn from the system for the following calculation.

Number of Years	pH	pe	Amount solubilized (mol)		
			U	Np	Pu
Case I					
1	7.1	2.2	5.10 <sup>-4</sup>	1.10 <sup>-13</sup>	4.10 <sup>-15</sup>
260	7.1	2.2	0.1	3.10 <sup>-11</sup>	1.10 <sup>-12</sup>
960	7.1	2.2	0.4	9.10 <sup>-11</sup>	3.10 <sup>-12</sup>
9960	7.8	13.2	1.3	8.1	4.10 <sup>-6</sup>
10 <sup>5</sup>	7.2	13.6	44.	10.9	3.10 <sup>-5</sup>
10 <sup>6</sup>	7.1	13.4	462.	-	7.10 <sup>-5</sup>
Total amounts (mol)			507.	19.	1.10 <sup>-4</sup>
Case II					
260	7.1	2.2	0.13	3.10 <sup>-11</sup>	1.10 <sup>-12</sup>
960	7.1	2.2	0.36	9.10 <sup>-11</sup>	3.10 <sup>-12</sup>
9960	7.1	2.2	3.4	1.10 <sup>-9</sup>	4.10 <sup>-11</sup>
10 <sup>5</sup>	7.2	1.7	19.2	2.10 <sup>-8</sup>	5.10 <sup>-10</sup>
10 <sup>6</sup>	7.4	1.3	120.	2.10 <sup>-7</sup>	7.10 <sup>-9</sup>
Total amounts (mol)			143.	2.10 <sup>-7</sup>	8.10 <sup>-9</sup>



Table 6. Main soluble complexes and solid phases for the system: matrix and 2mM bicarbonate solution. Case I.

Component	Years:	
	960 (pH=7.1, pe=2.2)	10 <sup>5</sup> (pH=7.2, pe=13.6)
U	(UO <sub>2</sub> ) <sub>3</sub> (CO <sub>3</sub> ) <sub>6</sub> <sup>6-</sup> , UO <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> <sup>4-</sup> UO <sub>2</sub> (s), UO <sub>2</sub> (OH) <sub>2</sub> (s)	(UO <sub>2</sub> ) <sub>3</sub> (CO <sub>3</sub> ) <sub>6</sub> <sup>6-</sup> , UO <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> <sup>4-</sup> UO <sub>2</sub> (OH) <sub>2</sub> (s)
Np	Np(OH) <sub>5</sub> <sup>-</sup> , NpO <sub>2</sub> (s)	NpO <sub>2</sub> <sup>+</sup> , NpO <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> <sup>4-</sup> , NpO <sub>2</sub> OH(aq)
Pu	Pu(OH) <sub>5</sub> <sup>-</sup> , PuO <sub>2</sub> (s)	PuO <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> <sup>4-</sup> , PuO <sub>2</sub> (s)

In case I, the initial low value of the redox potential increases strongly after about 2000 years. This is due to a complete oxidation of UO<sub>2</sub>(s) to UO<sub>2</sub>(OH)<sub>2</sub>(s). A fairly large amount of uranium, about 10% of the total inventory, has been solubilized during a 10<sup>6</sup> year period. At the same time, all neptunium but very little plutonium has gone into solution.

The amounts of oxidants produced in case II are much lower than in I. For case II this results in fairly low equilibrium values of pe during the whole 10<sup>6</sup> year period, with a very low mobilization of both neptunium and plutonium. One observes from Table 5, that the amounts of uranium solubilized is of the same order of magnitude both in case I and II. This is due to the fact that the soluble uranium species are dominated by uranium(VI) carbonate complexes over a very broad pe-range.

From Table 7, it is obvious that the total carbonate concentration is the main factor determining the amount of solubilization under radiolysis conditions. A doubling of the

total carbonate concentrations leads approximately to twice the amounts of dissolved uranium and plutonium. At zero, carbonate concentration, all neptunium, but only very small amounts of uranium and plutonium, are dissolved. An increase in the flow rate will have approximately the same effect as an increase in the carbonate concentration. The main soluble species and solid phases formed are given in Table 6.

Table 7. Influence of total carbonate concentration in the calculations for the system: matrix and bicarbonate solution. Time:  $10^6$  years. Case I.

HCO <sub>3</sub> <sup>-</sup> Tot. conc.(mM)	pH	pe	Total amount solubilized (mol)		
			U	Np	Pu
0.0	8.96	11.7	0.044	19.	$3 \cdot 10^{-7}$
2.0	7.13	13.5	461.	19.	$1 \cdot 10^{-4}$
4.0	7.04	13.6	1240.	19.	$2 \cdot 10^{-4}$

The equilibrium model used here should result in an overestimation of the amounts of the actinides that have been solubilized. One reason is the formation of protective layers of uranium peroxide,  $UO_4(s)$ , and "intermediate" oxide phases, e.g.  $U_3O_8(s)$  and  $UO_2(OH)_2(s)$ . The formation of surface films of this materials is well-known from studies of defects in nuclear fuels and from electrochemical studies of  $UO_2(s)$  [3, 4].

There are some circumstantial evidences to support the conclusions obtained from the equilibrium calculations. Fuel

defects in power reactors [5] have resulted in a substantial increase in the neptunium activity in the primary water circuit but without any evidence for uranium dissolution and reprecipitation as crud. The water does not contain any carbonate. These observations refer to much higher temperatures than our calculations, still the experimental observations are in qualitative agreement with these model calculations.

Several studies of the OKLO phenomenon have indicated a very low mobility of uranium even in the presence of considerable radiolysis [6]. This finding may be correlated with the low carbonate concentration found in fluid inclusions which presumably keep a record of the composition of the fluid phase during the criticality period of the various reactor zones [6].

The solubilization of plutonium is of importance for any safety analysis. Our data indicate that only negligible amounts of this element are solubilized under equilibrium conditions.  $\text{UO}_2(\text{s})$  is a very efficient reductant for plutonium(VI). These conclusions are supported by the fact that no plutonium migration has been observed in OKLO [6].

One can imagine a non-equilibrium process where both U, Np and Pu are brought into solution in the penta- and hexavalent oxidation states. A reprecipitation may occur at a later stage, either on the surface of the  $\text{UO}_2$ -matrix, or at some distance from the canister. It is impossible to make any statements of the likelihood of such processes, an experimental verification is necessary. The situation is different in the

far field region, where we may rely on well established geologic evidence for the reduction of uranium(VI) by reducing minerals. Several such minerals are present in deep bed rocks and it is thus very likely that mobile actinoids in high oxidation states will ultimately be reduced, possibly by the formation of "redox-fronts" as discussed by Neretnieks et al. [7].

The precipitation of uranium(IV) oxide hydrate at the redox front will result in a co-precipitation also of other actinoids, e.g. Pu(III) and Np(V). The net effect of the co-precipitation is that the concentrations of the other actinoids in solution will be smaller than the values calculated from the thermodynamic data base.

A more detailed discussion together with some experimental data are presented in Appendix 2.

The solubility of actinoids is strongly dependent on the redox potential and a convenient way of visualizing the reprecipitation conditions is in the form of solubility -  $p_e$  diagrams as shown in Figure 2. From this Figure, one can easily decide the minimum redox potential that the geological formation must have in order to be acceptable from the actinoid migration point of view.

The quality of the equilibrium data used varies considerably. The most important quantities are the redox data and the solubility products for the oxide phases of the actinides.

An estimate of how sensitive our conclusions are for a variation in some solubility products and other equilibrium constants are given in Table 8. These data show that variations of the equilibrium constants for the predominating equilibria do not result in very large changes in the amounts of actinoids mobilized.

In the long time run, all  $\text{UO}_2(\text{s})$  is transformed into  $\text{UO}_2(\text{OH})_2(\text{s})$ , hence, the value of the solubility product of  $\text{UO}_2(\text{s})$  does not influence the amount of uranium solubilized. This conclusion is not valid for the short time periods, where solid  $\text{UO}_2$  is present in the system.

Table 8. Influence of some equilibrium constants<sup>a</sup> in the results of the calculations for the system: matrix and 2mM bicarbonate solution. Time:  $10^6$  years. Case I.

logarithm of:				pH	pe	Amount solubilized (mol)		
$k_1^a$	$k_2^a$	$k_3^a$	$k_4^a$			U	Np	Pu
-5.6 <sup>b</sup>	1.8 <sup>b</sup>	23.8 <sup>b</sup>	60.1 <sup>b</sup>	7.1	13.5	461	19	$1 \cdot 10^{-4}$
-6.6	1.8	23.8	60.1	7.8	12.8	1280	19	$2 \cdot 10^{-5}$
-5.6	2.8	23.8	60.1	7.1	13.5	461	19	$1 \cdot 10^{-4}$
-5.6	1.8	21.8	60.1	7.9	12.8	515	19	$8 \cdot 10^{-4}$
-5.6	1.8	23.8	66.0	8.6	12.1	854	19	$6 \cdot 10^{-6}$

a:

$$k_1 = \{\text{UO}_2(\text{OH})_2(\text{s})\} \{\text{H}^+\}^2 / \{\text{UO}_2^{2+}\}$$

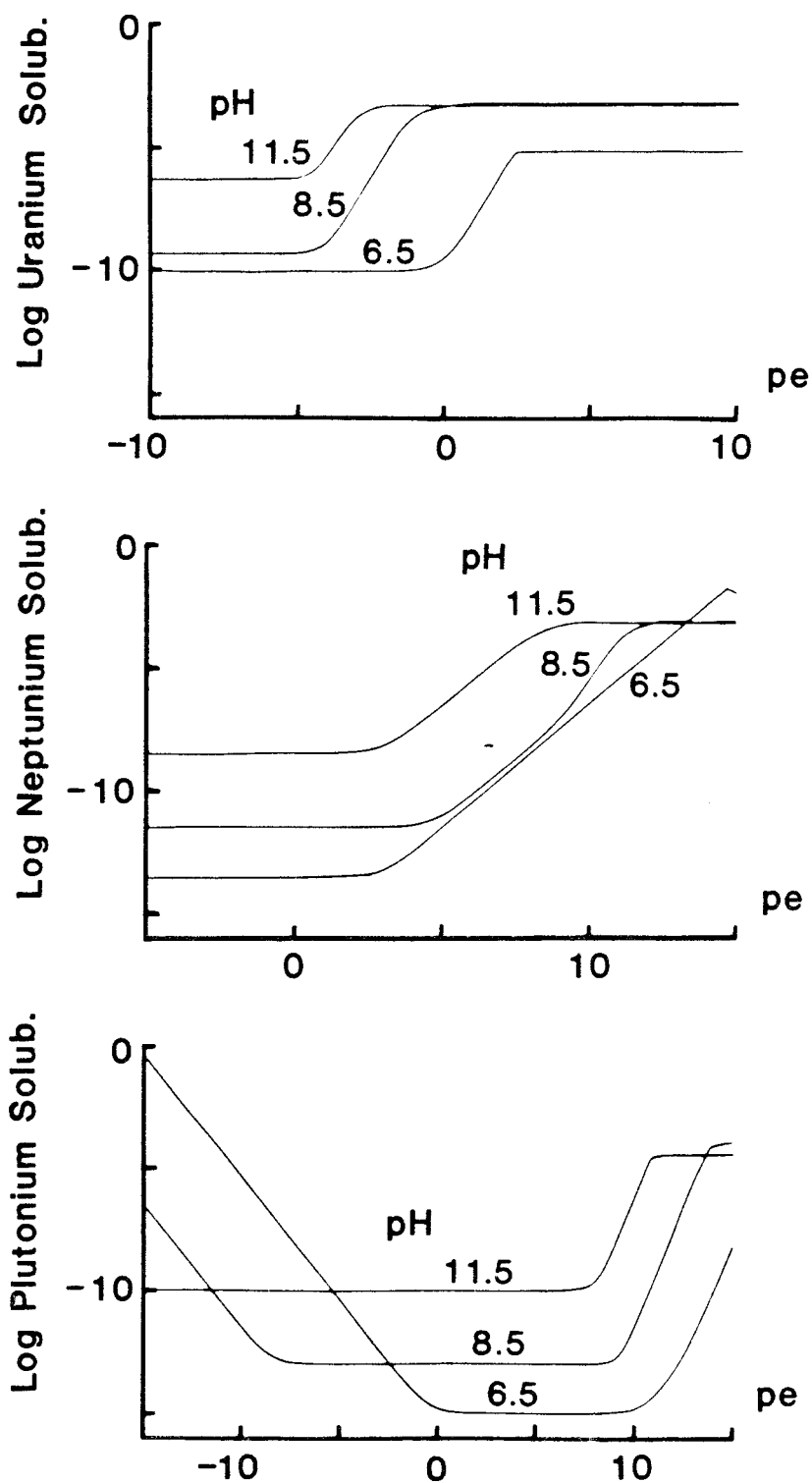
$$k_2 = \{\text{UO}_2(\text{s})\} \{\text{H}^+\}^4 / \{\text{U}^{4+}\}$$

$$k_3 = \{\text{UO}_2(\text{CO}_3)_3^{4-}\} / \{\text{UO}_2^{2+}\} \{\text{CO}_3^{2-}\}^3$$

$$k_4 = \{(\text{UO}_2)_3(\text{CO}_3)_6^{6-}\} / \{\text{UO}_2^{2+}\}^3 \{\text{CO}_3^{2-}\}^6$$

b: these are the values used throughout the report (compare with Table 7).

Figure 2. Log solubility vs pe curves for uranium, neptunium and plutonium. The calculations have been made at a total carbonate concentration of 2 mM and different values of pH. The data base used is given in Appendix 1. No data for neptunium(III) are included, hence, the calculations are only valid for  $pe > -5$ , i.e. a redox potential larger than -300 mV.



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## Appendix 1

### THE SELECTED THERMODYNAMIC DATA BASE FOR THE ACTINOID -H<sub>2</sub>O-CO<sub>2</sub>(g) SYSTEMS

Thermodynamic models are not better than the quality of the data base used and the experimental determination and/or the selection of these data from the literature is thus an important task.

Thermodynamic data always refer to a chosen standard state, for solutes this standard state is often the infinite dilute aqueous solution. However, data for many equilibria cannot be determined accurately, or at all, in dilute solution. This is invariably true for equilibria involving ions of high charge, e.g. most actinoid species. Precise thermodynamic information for these systems can only be obtained in the presence of an inert electrolyte of fairly high concentration (0.5 - 4 M) in order to ensure that activity factors are reasonably constant or estimable. This is the only possibility to unravel a complicated chemical equilibrium system. We are then faced with the problem of converting these data to zero ionic strength. Two common procedures are:

- calculation of the equilibrium constant as a function of ionic strength by using the "empirical" Davies equation.
- calculation of activity factors as a function of the ionic composition by using semi-theoretical electrolyte models, as used e.g. by Baes and Mesmer<sup>1</sup>.



## THE ESTIMATION OF ACTIVITY COEFFICIENTS

The Debye-Hückel term, which is the dominant term in the expression for the activity coefficients in dilute solution, accounts for long range electrostatic interactions. At higher concentration also short range non-electrostatic interactions have to be taken into account. This is usually made by adding ionic strength dependent terms to the Debye-Hückel expression. The methodology was first outlined by Brønsted<sup>2</sup> and later elaborated by Guggenheim<sup>3</sup> and Scatchard<sup>4</sup>. The basic assumptions in the so called specific ion interaction theory (referred to as S.I. theory) are:

- o the activity factor,  $\gamma_j$ , of an ion of charge  $z_j$  in a solution of the ionic strength  $I$  may be described by the equation

$$\log \gamma_j = -z_j^2 D + \sum_k \varepsilon(j,k,I) m_k \quad (1)$$

where

$D = 0.5107 / I(1 + 1.5\sqrt{I})^{-1}$  is the Debye-Hückel term at 25 °C.

The summation extends over all ions,  $k$ , present in solution with the molality  $m_k$ .

- o the interaction coefficients  $\varepsilon$  are zero for ions of the same charge sign.

By using (1), one can make fairly accurate estimates of ionic activity coefficients in mixtures of electrolytes, provided the interaction coefficients are known. Interaction coefficients involving simple ions can usually be determined from tabulated data of mean activity coefficients of electrolytes or from the corresponding osmotic coefficients. Interaction coefficients for complexes must be either estimated

from the charge and size of the ion or determined experimentally. This point will be discussed in the next section.

Strictly, the interaction coefficients are not constants. Their concentration dependence varies with the charge type and is small for 1:1, 1:2 and 2:1 electrolytes and can often be neglected at total molalities less than 3.5 m. This point has been emphasized by Guggenheim, who has presented a large experimental material supporting this approximation.<sup>3</sup> The concentration dependence is larger for electrolytes of higher charge type and in order to reproduce the activity coefficient data for these accurately, one must use concentration dependent interaction coefficients, c.f. Pitzer and Brewer<sup>5</sup> or Baes and Mesmer<sup>1</sup>.

By using a more elaborate virial expansion, Pitzer has managed to describe measured activity coefficient of a large number of pure electrolytes with a high precision over a large concentration range. Pitzer's model contains three parameters as compared to one in the S.I.-theory and seems to be difficult to use in equilibrium calculations concerning chemically complicated nuclear repository ground water systems.

The use of the S.I.-theory is demonstrated in some of our previous publications<sup>6,7</sup>. By using this semi-empirical theory, it seems possible to predict the values of thermodynamic quantities in dilute solutions from experimental measurements in concentrated electrolyte media. The quantitative success of these calculations depends on the accuracy of the interaction coefficients.

## ON THE MAGNITUDE OF INTERACTION COEFFICIENTS

Interaction coefficients can be calculated,<sup>8</sup> if mean activity coefficient data of the corresponding electrolytes are available.

It is possible to calculate interaction coefficients for complexes from equilibrium constant measurements at different ionic strengths, as shown in Ref. 6.

Since this procedure in general is not practical because of the very large experimental efforts involved, comparison of interaction coefficients of ions of the same charge type makes it possible to make reasonable estimations as shown from the following data

$$\begin{aligned} \epsilon(\text{HgCl}^+, \text{ClO}_4^-) &= 0.20; \quad \epsilon(\text{H}^+, \text{ClO}_4^-) = 0.14; \quad \epsilon(\text{YCO}_3^+, \text{ClO}_4^-) = 0.17 \\ \epsilon(\text{Cd}^{2+}, \text{ClO}_4^-) &= 0.36; \quad \epsilon(\text{Hg}^{2+}, \text{ClO}_4^-) = 0.30; \quad \epsilon(\text{YHCO}_3^{2+}, \text{ClO}_4^-) = 0.40 \\ \epsilon(\text{Fe}_2(\text{OH})_2^{4+}, \text{ClO}_4^-) &= 0.75; \quad \epsilon(\text{Y}_2\text{CO}_3^{4+}, \text{ClO}_4^-) = 0.80 \end{aligned}$$

The equilibrium constants do not depend too strongly on errors in the interaction coefficients. An error of  $\pm 0.1$  in the value of interaction coefficients of a complex will cause an error  $\pm 0.1 I$  in  $\log \beta_{pqr}^0$ , where  $I$  represents the ionic strength at which the constant is determined. These errors are in general much smaller than errors introduced by using "empirical" equations of the Davies type.

The ionic strength dependence of the interaction coefficients increases with the charge of ions and, furthermore, some experimental work must still be made to get an idea of the interaction coefficients of ions such as  $\text{U}(\text{CO}_3)_5^{6-}$ .

## THE THERMODYNAMIC DATA BASE

The thermodynamic data used by us is given in Table A1, and has its source in both compilations (Baes and Mesmer,<sup>1</sup> Lemire and Tremaine,<sup>9</sup> Charlot, Collumean and Marchon,<sup>10</sup> Sillén and Martell<sup>11</sup>) and some research papers (Bilinski and Schindler,<sup>12</sup> Grenthe et al.<sup>6,7,13-17</sup>). All data refers to 25 °C and 1 atm. In some cases, the original equilibrium constants were extrapolated to zero ionic strength by using the S.I.-theory.

No reliable experimental data are available on the stability constants of carbonato complexes of neptunium and plutonium in their various oxidation states. For the oxidation states +4, +5 and +6, we have assumed that these constants have the same values as the corresponding stability constants for uranium (IV,V and VI). The constants for the oxidation state +3 is in the same way modelled by the corresponding constants for the trivalent lanthanoids. In view of the chemical similarities between the various actinoids, and between actinoids and lanthanoids we expect that the errors introduced by this procedure will be fairly small (less than one order of magnitude).

The quality of the experimental thermodynamic data varies. At the present state of knowledge, most data are known with a precision better than two orders of magnitude. The largest uncertainties are found among the solubility products for the oxide/hydroxide phases of the actinoids. In a continuation of the present research program, we will undertake a critical examination and an experimental verification of some of these thermodynamic key data.

In order to obtain reliable information from the model calculations, it is necessary to include all possible species and their chemical compositions. However, there are some uncertainties referring to the composition of some predominant species

- o the composition of actinoid(V) carbonate species at low carbonate concentration is not known. The limiting complex is very likely  ${}^7\text{MO}_2(\text{CO}_3)_3^{5-}$ , but neither the stoichiometry, nor the equilibrium constants for the lower complexes are known. This lack of knowledge may affect the predicted behaviour of neptunium(V).
- o some mixed actinoid(III and VI) carbonate/hydroxide complexes have been reported in the literature. We have not been able to obtain an experimental confirmation of their existence in the pH -  $\text{pCO}_3$  range relevant for ground water. Hence, no data of this type have been included in the Table.

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Table A1. Thermodynamic data base for the actinoid-

		-H <sub>2</sub> O-CO <sub>2</sub> (g) systems. The input consists of an identification text, the equilibrium constant and the stoichiometric coefficients. Usually C stands for CO <sub>3</sub> <sup>2-</sup> , e.g. PuO2C3 4- stands for PuO <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub> <sup>4-</sup> , and UO2)3C6 6- stands for (UO <sub>2</sub> ) <sub>3</sub> (CO <sub>3</sub> ) <sub>6</sub> <sup>6-</sup> . The solid phases are given after the soluble species.						
9, 87, 17, 6,								
H+	,							
e-	,							
CO3 2-	,							
Cu(s)	,							
Zr(s)	,							
UO2(s)	,							
NpO2(s)	,							
PuO2(s)	,							
Pb(s)	,							
HCO3 -	,	10.329,	1.00,	0.00,	1.00,	0.00,	0.00,	0.00,
			0.00,	0.00,	0.00,			
H2CO3	,	16.681,	2.00,	0.00,	1.00,	0.00,	0.00,	0.00,
			0.00,	0.00,	0.00,			
OH-	,	-14.000,	-1.00,	0.00,	0.00,	0.00,	0.00,	0.00,
			0.00,	0.00,	0.00,			
O2(g)	,	-84.486,	-4.00,	-4.00,	0.00,	0.00,	0.00,	0.00,
			0.00,	0.00,	0.00,			
H2(g)	,	-1.389,	2.00,	2.00,	0.00,	0.00,	0.00,	0.00,
			0.00,	0.00,	0.00,			
Cu+	,	-8.790,	0.00,	-1.00,	0.00,	1.00,	0.00,	0.00,
			0.00,	0.00,	0.00,			
Cu 2+	,	-11.490,	0.00,	-2.00,	0.00,	1.00,	0.00,	0.00,
			0.00,	0.00,	0.00,			
CuOH +	,	-19.490,	-1.00,	-2.00,	0.00,	1.00,	0.00,	0.00,
			0.00,	0.00,	0.00,			
CuOH2	,	-28.790,	-2.00,	-2.00,	0.00,	1.00,	0.00,	0.00,
			0.00,	0.00,	0.00,			
CuOH3 -	,	-39.290,	-3.00,	-2.00,	0.00,	1.00,	0.00,	0.00,
			0.00,	0.00,	0.00,			
CuOH4 2-	,	-51.090,	-4.00,	-2.00,	0.00,	1.00,	0.00,	0.00,
			0.00,	0.00,	0.00,			
Cu2OH2 2+	,	-33.340,	-2.00,	-4.00,	0.00,	2.00,	0.00,	0.00,
			0.00,	0.00,	0.00,			
CuC	,	-4.720,	0.00,	-2.00,	1.00,	1.00,	0.00,	0.00,
			0.00,	0.00,	0.00,			
CuC2 2-	,	-1.480,	0.00,	-2.00,	2.00,	1.00,	0.00,	0.00,
			0.00,	0.00,	0.00,			
Zr 4+	,	94.790,	0.00,	-4.00,	0.00,	0.00,	1.00,	0.00,
			0.00,	0.00,	0.00,			
ZrOH 3+	,	95.090,	-1.00,	-4.00,	0.00,	0.00,	1.00,	0.00,
			0.00,	0.00,	0.00,			
ZrOH2 2+	,	93.070,	-2.00,	-4.00,	0.00,	0.00,	1.00,	0.00,
			0.00,	0.00,	0.00,			
ZrOH3 +	,	89.690,	-3.00,	-4.00,	0.00,	0.00,	1.00,	0.00,
			0.00,	0.00,	0.00,			
ZrOH4	,	85.090,	-4.00,	-4.00,	0.00,	0.00,	1.00,	0.00,
			0.00,	0.00,	0.00,			
ZrOH5 -	,	78.790,	-5.00,	-4.00,	0.00,	0.00,	1.00,	0.00,
			0.00,	0.00,	0.00,			
Zr3OH4 8+	,	283.770,	-4.00,	-12.00,	0.00,	0.00,	3.00,	0.00,
			0.00,	0.00,	0.00,			
Zr4OH8 8+	,	385.160,	-8.00,	-16.00,	0.00,	0.00,	4.00,	0.00,
			0.00,	0.00,	0.00,			
U 4+	,	-1.800,	4.00,	0.00,	0.00,	0.00,	0.00,	1.00,
			0.00,	0.00,	0.00,			
UOH 3+	,	-2.250,	3.00,	0.00,	0.00,	0.00,	0.00,	1.00,
			0.00,	0.00,	0.00,			
UOH2 2+	,	-4.400,	2.00,	0.00,	0.00,	0.00,	0.00,	1.00,
			0.00,	0.00,	0.00,			



UOH3 +	,	-7.600,	1.00,	0.00,	0.00,	0.00,	0.00,	1.00,
			0.00,	0.00,	0.00,			
UOH4	,	-11.900,	0.00,	0.00,	0.00,	0.00,	0.00,	1.00,
			0.00,	0.00,	0.00,			
UOH5 -	,	-17.800,	-1.00,	0.00,	0.00,	0.00,	0.00,	1.00,
			0.00,	0.00,	0.00,			
UC5 6-	,	34.700,	4.00,	0.00,	5.00,	0.00,	0.00,	1.00,
			0.00,	0.00,	0.00,			
UO2 +	,	-11.100,	0.00,	-1.00,	0.00,	0.00,	0.00,	1.00,
			0.00,	0.00,	0.00,			
UO2C3 5-	,	2.010,	0.00,	-1.00,	3.00,	0.00,	0.00,	1.00,
			0.00,	0.00,	0.00,			
UO2 2+	,	-12.960,	0.00,	-2.00,	0.00,	0.00,	0.00,	1.00,
			0.00,	0.00,	0.00,			
UO2OH +	,	-18.760,	-1.00,	-2.00,	0.00,	0.00,	0.00,	1.00,
			0.00,	0.00,	0.00,			
UO2)2OH2 2+,		-31.520,	-2.00,	-4.00,	0.00,	0.00,	0.00,	2.00,
			0.00,	0.00,	0.00,			
UO2)3OH5 +,		-54.510,	-5.00,	-6.00,	0.00,	0.00,	0.00,	3.00,
			0.00,	0.00,	0.00,			
UO2C	,	-4.360,	0.00,	-2.00,	1.00,	0.00,	0.00,	1.00,
			0.00,	0.00,	0.00,			
UO2)3OH)3C +,		-37.600,	-3.00,	-6.00,	1.00,	0.00,	0.00,	3.00,
			0.00,	0.00,	0.00,			
UO2)3C6 6-,		21.240,	0.00,	-6.00,	6.00,	0.00,	0.00,	3.00,
			0.00,	0.00,	0.00,			
UO2C3 4-	,	10.860,	0.00,	-2.00,	3.00,	0.00,	0.00,	1.00,
			0.00,	0.00,	0.00,			
Np 4+	,	-4.000,	4.00,	0.00,	0.00,	0.00,	0.00,	0.00,
			1.00,	0.00,	0.00,			
NpOH 3+	,	-5.500,	3.00,	0.00,	0.00,	0.00,	0.00,	0.00,
			1.00,	0.00,	0.00,			
NpOH5 -	,	-20.000,	-1.00,	0.00,	0.00,	0.00,	0.00,	0.00,
			1.00,	0.00,	0.00,			
NpC5 6-	,	32.500,	4.00,	0.00,	5.00,	0.00,	0.00,	0.00,
			1.00,	0.00,	0.00,			
NpO2 +	,	-16.510,	0.00,	-1.00,	0.00,	0.00,	0.00,	0.00,
			1.00,	0.00,	0.00,			
NpO2OH	,	-25.360,	-1.00,	-1.00,	0.00,	0.00,	0.00,	0.00,
			1.00,	0.00,	0.00,			
NpO2C3 5-	,	-3.400,	0.00,	-1.00,	3.00,	0.00,	0.00,	0.00,
			1.00,	0.00,	0.00,			
NpO2 2+	,	-35.780,	0.00,	-2.00,	0.00,	0.00,	0.00,	0.00,
			1.00,	0.00,	0.00,			
NpO2OH +	,	-40.930,	-1.00,	-2.00,	0.00,	0.00,	0.00,	0.00,
			1.00,	0.00,	0.00,			
NpO2)2OH2 2+,-		77.950,	-2.00,	-4.00,	0.00,	0.00,	0.00,	0.00,
			2.00,	0.00,	0.00,			
NpO2)3OH5 +,-		124.830,	-5.00,	-6.00,	0.00,	0.00,	0.00,	0.00,
			3.00,	0.00,	0.00,			
NpO2C	,	-27.200,	0.00,	-2.00,	1.00,	0.00,	0.00,	0.00,
			1.00,	0.00,	0.00,			
NpO2C3 4-	,	-12.000,	0.00,	-2.00,	3.00,	0.00,	0.00,	0.00,
			1.00,	0.00,	0.00,			
Pu 4+	,	-6.500,	4.00,	0.00,	0.00,	0.00,	0.00,	0.00,
			0.00,	1.00,	0.00,			
PuOH 3+	,	-7.000,	3.00,	0.00,	0.00,	0.00,	0.00,	0.00,
			0.00,	1.00,	0.00,			
PuOH2 2+	,	-8.800,	2.00,	0.00,	0.00,	0.00,	0.00,	0.00,
			0.00,	1.00,	0.00,			

PuOH3 +	, -11.800,	1.00,	0.00,	0.00,	0.00,	0.00,	0.00,
		0.00,	1.00,	0.00,			
PuOH4	, -16.000,	0.00,	0.00,	0.00,	0.00,	0.00,	0.00,
		0.00,	1.00,	0.00,			
PuOH5 -	, -21.500,	-1.00,	0.00,	0.00,	0.00,	0.00,	0.00,
		0.00,	1.00,	0.00,			
PuC5 6-	, 30.000,	4.00,	0.00,	5.00,	0.00,	0.00,	0.00,
		0.00,	1.00,	0.00,			
PuO2 +	, -25.500,	0.00,	-1.00,	0.00,	0.00,	0.00,	0.00,
		0.00,	1.00,	0.00,			
PuO2OH	, -35.200,	-1.00,	-1.00,	0.00,	0.00,	0.00,	0.00,
		0.00,	1.00,	0.00,			
PuO2C3 5-	, -12.400,	0.00,	-1.00,	3.00,	0.00,	0.00,	0.00,
		0.00,	1.00,	0.00,			
PuO2 2+	, -41.700,	0.00,	-2.00,	0.00,	0.00,	0.00,	0.00,
		0.00,	1.00,	0.00,			
PuO2OH +	, -47.300,	-1.00,	-2.00,	0.00,	0.00,	0.00,	0.00,
		0.00,	1.00,	0.00,			
PuO2)2OH2 2+,-91.800,		-2.00,	-4.00,	0.00,	0.00,	0.00,	0.00,
		0.00,	2.00,	0.00,			
PuO2)3OH5 +,-146.750,		-5.00,	-6.00,	0.00,	0.00,	0.00,	0.00,
		0.00,	3.00,	0.00,			
PuO2C	, -33.100,	0.00,	-2.00,	1.00,	0.00,	0.00,	0.00,
		0.00,	1.00,	0.00,			
PuO2C3 4-	, -17.900,	0.00,	-2.00,	3.00,	0.00,	0.00,	0.00,
		0.00,	1.00,	0.00,			
Pu 3+	, 10.600,	4.00,	1.00,	0.00,	0.00,	0.00,	0.00,
		0.00,	1.00,	0.00,			
PuOH 2+	, 2.600,	3.00,	1.00,	0.00,	0.00,	0.00,	0.00,
		0.00,	1.00,	0.00,			
PuOH3	, -16.400,	1.00,	1.00,	0.00,	0.00,	0.00,	0.00,
		0.00,	1.00,	0.00,			
PuOH4 -	, -27.400,	0.00,	1.00,	0.00,	0.00,	0.00,	0.00,
		0.00,	1.00,	-0.00,			
PuHC 2+	, 20.200,	5.00,	1.00,	1.00,	0.00,	0.00,	0.00,
		0.00,	1.00,	0.00,			
PuC +	, 15.600,	4.00,	1.00,	1.00,	0.00,	0.00,	0.00,
		0.00,	1.00,	0.00,			
PuC2 -	, 21.600,	4.00,	1.00,	2.00,	0.00,	0.00,	0.00,
		0.00,	1.00,	0.00,			
PuC3 3-	, 22.900,	4.00,	1.00,	3.00,	0.00,	0.00,	0.00,
		0.00,	1.00,	0.00,			
PuC4 5-	, 25.100,	4.00,	1.00,	4.00,	0.00,	0.00,	0.00,
		0.00,	1.00,	0.00,			
Pb 2+	, 4.260,	0.00,	-2.00,	0.00,	0.00,	0.00,	0.00,
		0.00,	0.00,	1.00,			
PbOH +	, -3.450,	-1.00,	-2.00,	0.00,	0.00,	0.00,	0.00,
		0.00,	0.00,	1.00,			
PbOH2	, -12.860,	-2.00,	-2.00,	0.00,	0.00,	0.00,	0.00,
		0.00,	0.00,	1.00,			
PbOH3 -	, -23.800,	-3.00,	-2.00,	0.00,	0.00,	0.00,	0.00,
		0.00,	0.00,	1.00,			
Pb3OH4 2+	, -11.100,	-4.00,	-6.00,	0.00,	0.00,	0.00,	0.00,
		0.00,	0.00,	3.00,			
Pb4OH4 4+	, -3.840,	-4.00,	-8.00,	0.00,	0.00,	0.00,	0.00,
		0.00,	0.00,	4.00,			
PbC2 2-	, 13.350,	0.00,	-2.00,	2.00,	0.00,	0.00,	0.00,
		0.00,	0.00,	1.00,			
PbC	, 9.700,	0.00,	-2.00,	1.00,	0.00,	0.00,	0.00,
		0.00,	0.00,	1.00,			

Pb(HC)2	,	29.700,	2.00,	-2.00,	2.00,	0.00,	0.00,	0.00,
			0.00,	0.00,	1.00,			
Pb(HC)3 -	,	40.400,	3.00,	-2.00,	3.00,	0.00,	0.00,	0.00,
			0.00,	0.00,	1.00,			
Cu2O(s)	,	-15.980,	-2.00,	-2.00,	0.00,	2.00,	0.00,	0.00,
			0.00,	0.00,	0.00,			
CuOH2(s)	,	-20.130,	-2.00,	-2.00,	0.00,	1.00,	0.00,	0.00,
			0.00,	0.00,	0.00,			
Cu2OH2C(s)	,	-20.460,	-2.00,	-4.00,	1.00,	2.00,	0.00,	0.00,
			0.00,	0.00,	0.00,			
ZrO2(s)	,	96.690,	-4.00,	-4.00,	0.00,	0.00,	1.00,	0.00,
			0.00,	0.00,	0.00,			
UO2OH2(s)	,	-18.560,	-2.00,	-2.00,	0.00,	0.00,	0.00,	1.00,
			0.00,	0.00,	0.00,			
UO2C(s)	,	0.660,	0.00,	-2.00,	1.00,	0.00,	0.00,	1.00,
			0.00,	0.00,	0.00,			
NpO2OH(s)	,	-21.210,	-1.00,	-1.00,	0.00,	0.00,	0.00,	0.00,
			1.00,	0.00,	0.00,			
NpO2OH2(s)	,	-42.380,	-2.00,	-2.00,	0.00,	0.00,	0.00,	0.00,
			1.00,	0.00,	0.00,			
NpO2C(s)	,	-22.000,	0.00,	-2.00,	1.00,	0.00,	0.00,	0.00,
			1.00,	0.00,	0.00,			
PuO2OH(s)	,	-30.900,	-1.00,	-1.00,	0.00,	0.00,	0.00,	0.00,
			0.00,	1.00,	0.00,			
PuO2OH2(s)	,	-44.700,	-2.00,	-2.00,	0.00,	0.00,	0.00,	0.00,
			0.00,	1.00,	0.00,			
PuO2C(s)	,	-27.900,	0.00,	-2.00,	1.00,	0.00,	0.00,	0.00,
			0.00,	1.00,	0.00,			
PuOH3(s)	,	-11.700,	1.00,	1.00,	0.00,	0.00,	0.00,	0.00,
			0.00,	1.00,	0.00,			
Pu2C3(s)	,	36.820,	8.00,	2.00,	3.00,	0.00,	0.00,	0.00,
			0.00,	2.00,	0.00,			
PbO(s)	,	-8.100,	-2.00,	-2.00,	0.00,	0.00,	0.00,	0.00,
			0.00,	0.00,	1.00,			
PbC(s)	,	16.500,	0.00,	-2.00,	1.00,	0.00,	0.00,	0.00,
			0.00,	0.00,	1.00,			
Pb3OH2C2(s)	,	29.300,	-2.00,	-6.00,	2.00,	0.00,	0.00,	0.00,
			0.00,	0.00,	3.00,			

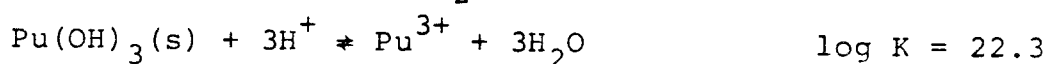
## Appendix 2

### CO-PRECIPITATION OF Pu(III) WITH UO<sub>2</sub>(s)

Uranium dioxide and its content of other actinoids may be solubilized in the near field region as a result of radiolysis. The solubilized actinoids will migrate and may ultimately reach a reducing far field region. The soluble uranium(VI) carbonate complexes will then be reduced to UO<sub>2</sub>(s) and other actinoids are expected to be co-precipitated. In order to test the degree of co-precipitation of tervalent actinoids, we have performed a series of precipitation experiments using plutonium(III) as a model substance.

### Thermodynamic data

Uranium(IV) and plutonium(IV) reacts in solution forming uranium(VI) and plutonium(III). Both U(IV) and Pu(III) forms sparingly soluble hydroxides. Baes and Mesmer [1] give the following data, valid at infinite dilution



### Experimental

Preparation of solutions etc. A 27 mM solution of <sup>235</sup>UO<sub>2</sub>(ClO<sub>4</sub>)<sub>2</sub> was reduced to U(IV) by H<sub>2</sub>(g) using a Pt/Pd catalyst. The <sup>239</sup>Pu(IV) stock solution was obtained from the Department of Nuclear Chemistry, Chalmers Institute of Technology.

Solutions in the following concentration intervals were prepared by mixing

$$[\text{HClO}_4] = 1 \text{ M}$$

$$19 \text{ mM} < [\text{U(IV)}] < 26.8 \text{ mM}$$

$$0.2 \text{ mM} < \text{Pu(III)} < 1 \text{ mM}$$

The total concentrations of some of the solutions used are given in Table A2, 1. The oxidation state of Pu was checked by the standard TTA (thenoyltrifluoroacetone) extraction technique [2].

Uranium(IV) oxide hydrate was precipitated by coulometric generation of  $\text{OH}^-$ . Initially a green precipitate was formed which on standing was transformed into a black solid. The solution with the precipitate was left for one week in order to ensure some recrystallization of the solid. The pH in the solution was monitored continuously.

A series of precipitations at different hydrogen ion concentrations were made, c.f. the Table. The equilibrium concentrations of  $\text{U}^{4+}$  and  $\text{Pu}^{3+}$  were measured using standard counting technique (184 keV  $\gamma$  for  $^{235}\text{U}$  and  $\alpha$ -counting for  $^{239}\text{Pu}$ . The latter quantity was corrected for the  $\alpha$ -activity of  $^{235}\text{U}$ ).

The relative amount of U and Pu in the solid phase were analyzed after dissolution in 1 M  $\text{HNO}_3$ .

### Results

From the equilibrium concentrations of  $\text{H}^+$ ,  $\text{U}^{4+}$  and  $\text{Pu}^{3+}$ , we can calculate a value of the quantities

$$\log [\text{U}^{4+}]/[\text{H}^+]^4$$

and

$$\log [\text{Pu}^{3+}]/[\text{H}^+]^3$$

these quantities are equal to the corresponding solubility products provided the activity of the solid phase is the same as for the pure phases. This applies in the case of  $\text{UO}_2(\text{s})$  where the activity of the solid phase is not affected because of the small amount of Pu present (< 5%).

In order to calculate the solubility product for  $\text{UO}_2(\text{s})$ , we need to calculate  $[\text{U}^{4+}]$  from the experimentally determined total concentration

$$[\text{U}(\text{IV})] = [\text{U}^{4+}] + [\text{U}(\text{OH})^{3+}] = [\text{U}^{4+}](1 + \beta_{11}/[\text{H}^+])$$

where  $\beta_{11}$  is the first hydrolysis constant of  $\text{U}^{4+}$  taken from Baes and Mesmer ( $\log \beta_{11} = -0.65$ ). The solubility product calculated from the data in Table A2,1 was equal to

$$\log K_s = 1.6 \pm 1.2$$

The error limit is fairly large and the average differs from the value given by Baes and Mesmer. Both these phenomena are probably due to an incomplete crystallinity of the solid phase. The less crystalline phases are more soluble than the phase quoted by Baes and Mesmer. This type of phenomenon is well known also for many other metal hydroxides.

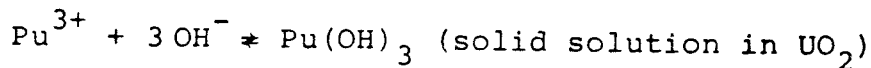
In the case of  $\text{Pu}(\text{OH})_3$ , we cannot expect that the dilute solid solution of  $\text{Pu}(\text{III})$  in  $\text{UO}_2$  has the same activity as pure  $\text{Pu}(\text{OH})_3$ , c.f. Garrels and Christ [3].

The ionic product for the plutonium case calculated from the tabulated data was equal to

$$\log [\text{Pu}^{3+}]/[\text{H}^+]^3 = -0.3 \pm 0.9$$

This value deviates considerably from the one valid for a pure phase of  $\text{Pu}(\text{OH})_3$ , i.e. the activity of the solid solution differs very much from unity. The net result of this is that the equilibrium concentration of plutonium is much smaller when a solid solution of  $\text{Pu}(\text{III})$  and  $\text{U}(\text{IV})$  is formed than when the solid is pure  $\text{Pu}(\text{OH})_3$ .

The experimental material obtained in this study does not permit a quantitative determination of the equilibrium constant for the reaction



because no information is available on the properties of the solid (e.g. whether it is best described as an ideal solution or a regular solution). However, it seems possible to make a semi-quantitative evaluation of the concentration of Pu(III) in solution, when the co-precipitation amounts to almost a few percent Pu(III). For this case, the "solubility product" is equal to

$$\log [\text{Pu}^{3+}]/[\text{H}^+]^3 \approx 0 \pm 2$$

Co-precipitation of Pu has also been tested by using  $^{237}\text{Pu}$ . Precipitation of  $\text{UO}_2$  from a solution which also contains less than  $10^{-10}$  M  $^{237}\text{Pu}$  resulted in an approximately 50% co-precipitation of the Pu activity.

Dissolution of the co-precipitated (U,Pu) oxide phase in carbonate containing water under oxidizing conditions

Part of the precipitated  $\text{UO}_2$  was agitated with 25 ml 5 mM  $\text{NaHCO}_3$  solution by passing a stream of air through the solution.

The concentrations of dissolved U and Pu were measured after 1 and 3 weeks.

The following results were obtained

1 week

$$[\text{U(VI)}] = 0.47 \cdot 10^{-3} \text{ M}$$

$$[\text{Pu}] = 2 \cdot 10^{-5} \text{ M}$$

3 weeks

$$[\text{U(VI)}] = 1.05 \cdot 10^{-3} \text{ M}$$

$$[\text{Pu}] = 3.1 \cdot 10^{-6} \text{ M}$$

It is obvious that uranium has dissolved under the formation of soluble uranium(VI) carbonate complexes, while plutonium to a large extent remains in the solid form, probably as plutonium(IV) oxide. These experimental findings give a qualitative confirmation of the equilibrium calculations presented in the main section of this report.

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