

# SOLUBILITIES OF Am, U, Np AND Pu IN GRANITIC GROUNDWATER

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**Abstract :** The solubilities of Am, U, Np and Pu in granitic groundwater were calculated using geochemical codes with recent thermodynamic data selected from literatures. Calculated solubilities were compared to the experimental data from the leaching test with spent UO<sub>2</sub> fuel in the respective solution without and with iron powder under an Ar-CO<sub>2</sub> atmosphere of 0.03% carbon dioxide gas.

The calculated solubilities of americium and uranium in the solution without iron powder were found to be in agreement with experimental data, but those of neptunium and plutonium did not match the measured data due to the non-equilibrium effects such as colloid formation or radiolytic oxidation. The measured concentrations of actinides in the solution with iron powder were much lower than what were predicted. This was attributed to the adsorption onto the corroded iron surface or co-precipitation.

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**Key Words :** Solubility, actinides, Am, U, Np, Pu, granitic groundwater

## INTRODUCTION

The geological disposal in deep bedrock repositories is a preferred option for the management of high-level radioactive waste (HLW). Most safety assessments for radioactive waste disposal use the concept of solubility limits as source terms to estimate the potential release of actinides and other radionuclides from the repository.<sup>1)</sup> Actinides have gained much attention in the safety assessment of HLW disposal due to their radiological toxicity and long half-lives. It is known that the solubility of actinides depends strongly on the composition of the groundwater in contact with the HLW. In the

last decade, many research groups investigated the solubilities of actinides in the composition of groundwater sampled from reference sites in crystalline rock for HLW disposal.<sup>2-9)</sup> When considering the studies for a single type of groundwater, e.g. granitic groundwater, there is a large range of calculated actinides solubilities, despite similarities in the chemical conditions studied. Discrepancies in actinides solubilities are attributed to the thermodynamic database used and the choice of the solubility limiting solid phase. In most studies the applied thermodynamic data are not fully listed in the open literature, and thus we cannot identify the exact reasons for the discrepancies observed. Although there are numerous thermodynamic databases,<sup>10-12)</sup> only a few studies<sup>13-16)</sup> have presented a set of well-documented thermodynamic data after critical reviews. A thermodynamic

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database represents a survey of what is known at a particular time. It should be therefore continuously upgraded to build a consensus of thermodynamic data involved in solubility calculation.

In order to establish confidence in the database, model calculations were applied to experimental data on the HLW interaction with the respective groundwater. Recently, a series of long-term leaching experiments of spent nuclear fuel were carried out.<sup>17)</sup> In the present study speciation and solubility of Am, U, Np and Pu for the conditions of the leaching experiments with granitic groundwater were analyzed by means of geochemical model.

## EXPERIMENTAL DATA

Leaching experiments<sup>17)</sup> were conducted in hot cells at Institute for Nuclear Waste Management Research Center, Karlsruhe, Germany, to study the behaviors of a powdered spent UO<sub>2</sub> fuel in a synthetic granitic groundwater that simulated a deep groundwater equilibrated with granite and fracture filling minerals (Table 1). The leaching experiments were carried out parallel with the addition of iron powder and without iron powder at the ambient temperature and the Ar-CO<sub>2</sub> atmosphere with the carbon dioxide of 0.03%. Since sampling in the hot cells was rather complicated, solutions were sampled only three times during the experiments. Aliquots of the sampled solutions were filtered through 450 nm and 1.8 nm membrane filters before analyzing the concentration of the solution. Differences in the measured concentrations of both filtered solutions were interpreted as the amount of colloidal bound actinide species. The measured pH, Eh and actinide concentration of each sample are given in Table 2. The measured Eh values indicate that all the solutions were oxidizing, except S6 (Eh = -0.54V). The Eh value in the solution with iron powder (S4 to S6) decreased with reaction time, which was probably caused by the oxidation of the iron powder. Taking into account that the Eh mea-

Table 1. Compositions of synthetic equilibrium granitic groundwater used in this study

Species	Composition Synthetic Equilibrium Granite Groundwater (mol/L)
Na <sup>+</sup>	4.1 × 10 <sup>-3</sup>
K <sup>+</sup>	5.1 × 10 <sup>-5</sup>
Ca <sup>++</sup>	6.0 × 10 <sup>-5</sup>
SiO <sub>2</sub>	2.1 × 10 <sup>-3</sup>
Cl <sup>-</sup>	2.9 × 10 <sup>-3</sup>
HCO <sub>3</sub> <sup>-</sup>	4.6 × 10 <sup>-4</sup>
F <sup>-</sup>	3.0 × 10 <sup>-4</sup>
pH	8.7
Eh(V)	0.25
Temp. (°C)	25

surement is uncertain under radiolytic conditions (i.e. redox disequilibrium), the measured Eh is considered as a semi-qualitative indicator representing the oxidative/reducing condition at the sampling time. The studied actinides display different release behaviors with reaction time. For examples, no significant change is observed in concentrations of Np and Pu measured after 1.8nm-ultrafiltration, while the concentration of Am for Samples S4 to S6 after 1.8nm-ultrafiltration increased with reaction time. Measured concentrations after 450nm filtration display a similar concentration vs. time pattern.

## GEOCHEMICAL CODE AND THERMODYNAMIC DATA

Solubility calculation was carried out using the geochemical code MUGREM that can deal with a multi-geochemical equilibrium reaction system including aqueous complexation reactions, precipitation-dissolution reactions as well as adsorption reactions, and was verified through comparisons with calculation results by other codes.<sup>18,19)</sup> The speciation plots were drawn by the Geochemists Workbench code.<sup>20)</sup>

Aqueous complex formation and solubility constants of actinides used in the present study are listed in Table 3. Most of the reaction constants were taken from the OECD/NEA thermodynamic database.<sup>13-15)</sup> Thermodynamically meaningful solubility requires the information of a well-defined solid phase style. Stable solids of

Table 2. Measured concentration from leaching test of spent UO<sub>2</sub> fuel powder<sup>17)</sup>

Sample a <sup>(a)</sup>	Actinide	Am (mol/L)	U (mol/L)	Np (mol/L)	Pu (mol/L)
S1 (49 days, pH= 8, Eh= 0.42V) <sup>(c)</sup>		1x10 <sup>-9</sup> <sup>(b)</sup> (3x10 <sup>-11</sup> )	5x10 <sup>-5</sup> (3x10 <sup>-5</sup> )	3x10 <sup>-8</sup> (3x10 <sup>-8</sup> )	3x10 <sup>-7</sup> (1x10 <sup>-8</sup> )
S2 (201days, pH =7.96, Eh =0.34V)		2x10 <sup>-8</sup> (4x10 <sup>-11</sup> )	2x10 <sup>-5</sup> (2x10 <sup>-6</sup> )	2x10 <sup>-8</sup> (6x10 <sup>-9</sup> )	3x10 <sup>-6</sup> (3x10 <sup>-8</sup> )
S3 (545days, pH =7.21, Eh= 0.38V)		4x10 <sup>-8</sup> (4x10 <sup>-11</sup> )	2x10 <sup>-5</sup> (6x10 <sup>-7</sup> )	8x10 <sup>-8</sup> (6x10 <sup>-8</sup> )	4x10 <sup>-6</sup> (4x10 <sup>-8</sup> )
S4 (50days, pH= 8.8 , Eh= 0.41V)		2x10 <sup>-9</sup> (3x10 <sup>-13</sup> )	9x10 <sup>-7</sup> (5x10 <sup>-8</sup> )	1x10 <sup>-9</sup> (1x10 <sup>-10</sup> )	1x10 <sup>-8</sup> (3x10 <sup>-11</sup> )
S5 (196days, pH =10, Eh= 0.28V)		4x10 <sup>-12</sup> (1x10 <sup>-12</sup> )	2x10 <sup>-8</sup> (2x10 <sup>-10</sup> )	1x10 <sup>-10</sup> (1x10 <sup>-10</sup> )	1x10 <sup>-10</sup> (4x10 <sup>-11</sup> )
S6 (545days, pH= 9.95, Eh= -0.54V)		2x10 <sup>-11</sup> (2x10 <sup>-11</sup> )	7x10 <sup>-8</sup> (4x10 <sup>-9</sup> )	3x10 <sup>-10</sup> (3x10 <sup>-10</sup> )	9x10 <sup>-11</sup> (1x10 <sup>-11</sup> )

(a): S1 to S3: without the addition of iron powder, S4 to S6: with the addition of iron powder of 2.68g

(b): after 450nm microfiltration (after 1.8nm ultrafiltration.)

(c): reaction time, measured pH and Eh, respectively

actinides in natural granite groundwater are usually known to be hydroxides, oxides, silicates and carbonates. Actinide solids and their solubility-product used in this study are listed in Table 4. Reaction constants different from the OECD/NEA thermodynamic database were selected through a review of recent literature. The compilation of the present thermodynamic data can be characterized as follows:

- The solubility product of AmOHCO<sub>3</sub>(s)<sup>21)</sup> used in the present work is a log unit 1.5 less than the OECD/NEA data.<sup>14)</sup>
- Reaction constants of Np(IV) and Pu(IV) hydroxo-carbonate complexes are incorporated. Recently, Neck and Kim<sup>22)</sup> observed by the laser induced breakdown spectroscopy (LIBS) that the ternary complexes of Np(IV) and Pu(IV) were predominant in neutral and alkaline regions. In the previous works those ternary species were not considered due to no clear experimental evidence.<sup>23)</sup>
- The actinide hydrolysis species An(OH)<sub>5</sub><sup>-</sup> (An denotes actinide) of tetravalent U, Np and Pu were omitted as there is no experimental evidence until now.
- The polynuclear ternary complexes of U(VI), for example (UO<sub>2</sub>)<sub>2</sub>CO<sub>3</sub>OH<sup>-</sup>, were not considered because the existence of the species is ambiguous although these species are accepted in the NEA-TDB.<sup>14)</sup> These species usually originate from potentiometric titration experiments under conditions exceeding the solubility. Under such over saturation conditions it is questionable whether well-defined species will be formed. The ternary complexes observed in the experiment are suggested to be colloids of varying composition.
- The formation constant of hydrolysis species and the solubility product of tetravalent actinide solids were taken from a literature for consistency.<sup>24)</sup> According to their study, the formation constants of hydrolysis species were preferentially selected from experimental studies at trace concentrations, where the interference of colloid formation could be excluded, and unknown formation constants of mononuclear complexes without experi-

Table 3. Complex formation constant of actinides used in this study

Actinides	Reaction	log $\beta$	Ref.	
<b>Americium III</b>	$\text{Am}^{3+} + \text{H}_2\text{O} - \text{H}^+ = \text{AmOH}^{2+}$	-7.30	21	
	$\text{Am}^{3+} + 2\text{H}_2\text{O} - 2\text{H}^+ = \text{Am}(\text{OH})_2^+$	-15.19	21	
	$\text{Am}^{3+} + 3\text{H}_2\text{O} - 3\text{H}^+ = \text{Am}(\text{OH})_3$	-25.69	15	
	$\text{Am}^{3+} + \text{F}^- = \text{AmF}^{2+}$	3.40	15	
	$\text{Am}^{3+} + 2\text{F}^- = \text{AmF}_2^+$	5.80	15	
	$\text{Am}^{3+} + \text{NO}_3^- = \text{AmNO}_3^{2+}$	1.33	15	
	$\text{Am}^{3+} + \text{Cl}^- = \text{AmCl}^{2+}$	0.24	30	
	$\text{Am}^{3+} + 2\text{Cl}^- = \text{AmCl}_2^+$	-0.74	30	
	$\text{Am}^{3+} + \text{SO}_4^{2-} = \text{AmSO}_4^+$	3.25	30	
	$\text{Am}^{3+} + 2\text{SO}_4^{2-} = \text{Am}(\text{SO}_4)_2^-$	3.70	30	
	$\text{Am}^{3+} + \text{CO}_3^{2-} = \text{AmCO}_3^+$	8.10	21	
	$\text{Am}^{3+} + 2\text{CO}_3^{2-} = \text{Am}(\text{CO}_3)_2^-$	13.00	21	
	$\text{Am}^{3+} + 3\text{CO}_3^{2-} = \text{Am}(\text{CO}_3)_3^{3-}$	15.20	21	
	$\text{Am}^{3+} + 4\text{CO}_3^{2-} = \text{Am}(\text{CO}_3)_4^{5-}$	13.00	21	
	<b>Uranium III</b>	$\text{U}^{4+} + \text{e}^- = \text{U}^{3+}$	-9.35	14
<b>IV</b>		$\text{U}^{4+} + \text{H}_2\text{O}(\text{l}) - \text{H}^+ = \text{UOH}^{3+}$	-0.40	24
		$\text{U}^{4+} + 2\text{H}_2\text{O}(\text{l}) - 2\text{H}^+ = \text{U}(\text{OH})_2^{2+}$	-1.09	24
		$\text{U}^{4+} + 3\text{H}_2\text{O}(\text{l}) - 3\text{H}^+ = \text{U}(\text{OH})_3^+$	-4.69	24
		$\text{U}^{4+} + 4\text{H}_2\text{O}(\text{l}) - 4\text{H}^+ = \text{U}(\text{OH})_4$	-9.99	24
		$6\text{U}^{4+} + 15\text{H}_2\text{O}(\text{l}) - 15\text{H}^+ = \text{U}_6(\text{OH})_{15}^{9+}$	-16.90	14
		$\text{U}^{4+} + \text{F}^- = \text{UF}^{3+}$	9.28	14
		$\text{U}^{4+} + 2\text{F}^- = \text{UF}_2^{2+}$	16.20	14
		$\text{U}^{4+} + \text{Cl}^- = \text{UCl}^{3+}$	1.72	14
		$\text{U}^{4+} + \text{SO}_4^{2-} = \text{USO}_4^{2+}$	6.50	14
		$\text{U}^{4+} + \text{NO}_3^- = \text{UNO}_3^{3+}$	1.47	14
		$\text{U}^{4+} + \text{CO}_3^{2-} = \text{UCO}_3^{2+}$	13.70	22
		$\text{U}^{4+} + 2\text{CO}_3^{2-} = \text{U}(\text{CO}_3)_2^0$	24.30	22
		$\text{U}^{4+} + 3\text{CO}_3^{2-} = \text{U}(\text{CO}_3)_3^{2-}$	31.90	22
		$\text{U}^{4+} + 4\text{CO}_3^{2-} = \text{U}(\text{CO}_3)_4^{4-}$	35.10	14
	$\text{U}^{4+} + 5\text{CO}_3^{2-} = \text{U}(\text{CO}_3)_5^{6-}$	34.00	14	
$\text{U}^{4+} + 3\text{H}_2\text{O}(\text{l}) - 3\text{H}^+ + \text{CO}_3^{2-} = \text{U}(\text{OH})_3\text{CO}_3^-$	-1.00	14		
<b>V</b>	$\text{U}^{4+} + 2\text{H}_2\text{O}(\text{l}) - 4\text{H}^+ - \text{e}^- = \text{UO}_2^+$	-7.55	14	
<b>VI</b>	$\text{U}^{4+} + 2\text{H}_2\text{O}(\text{l}) - 4\text{H}^+ - 2\text{e}^- = \text{UO}_2^{2+}$	-9.04	14	
	$\text{U}^{4+} + 3\text{H}_2\text{O}(\text{l}) - 5\text{H}^+ - 2\text{e}^- = \text{UO}_2\text{OH}^+$	-14.74	34	
	$\text{U}^{4+} + 4\text{H}_2\text{O}(\text{l}) - 6\text{H}^+ - 2\text{e}^- = \text{UO}_2(\text{OH})_2(\text{aq})$	-21.14	34	
	$\text{U}^{4+} + 5\text{H}_2\text{O}(\text{l}) - 7\text{H}^+ - 2\text{e}^- = \text{UO}_2(\text{OH})_3^-$	-29.04	34	
	$\text{U}^{4+} + 6\text{H}_2\text{O}(\text{l}) - 8\text{H}^+ - 2\text{e}^- = \text{UO}_2(\text{OH})_4^{2-}$	-41.44	34	
	$2\text{U}^{4+} + 6\text{H}_2\text{O}(\text{l}) - 10\text{H}^+ - 4\text{e}^- = (\text{UO}_2)_2(\text{OH})_2^{2+}$	-23.78	34	
	$3\text{U}^{4+} + 11\text{H}_2\text{O}(\text{l}) - 17\text{H}^+ - 6\text{e}^- = (\text{UO}_2)_3(\text{OH})_5^+$	-42.91	34	
	$3\text{U}^{4+} + 13\text{H}_2\text{O}(\text{l}) - 19\text{H}^+ - 6\text{e}^- = (\text{UO}_2)_3(\text{OH})_7^-$	-58.61	34	
	$\text{U}^{4+} + 2\text{H}_2\text{O}(\text{l}) - 4\text{H}^+ - 2\text{e}^- + \text{Cl}^- = \text{UO}_2\text{Cl}^+$	-8.87	34	
	$\text{U}^{4+} + 2\text{H}_2\text{O}(\text{l}) - 4\text{H}^+ - 2\text{e}^- + \text{SO}_4^{2-} = \text{UO}_2\text{SO}_4$	-5.79	34	
	$\text{U}^{4+} + 2\text{H}_2\text{O}(\text{l}) - 4\text{H}^+ - 2\text{e}^- + \text{F}^- = \text{UO}_2\text{F}^+$	-3.95	34	
	$\text{U}^{4+} + 2\text{H}_2\text{O}(\text{l}) - 4\text{H}^+ - 2\text{e}^- + 2\text{F}^- = \text{UO}_2\text{F}_2$	-0.42	34	
	$\text{U}^{4+} + 2\text{H}_2\text{O}(\text{l}) - 4\text{H}^+ - 2\text{e}^- + 3\text{F}^- = \text{UO}_2\text{F}_3^-$	1.86	34	
	$\text{U}^{4+} + 2\text{H}_2\text{O}(\text{l}) - 4\text{H}^+ - 2\text{e}^- + \text{CO}_3^{2-} = \text{UO}_2\text{CO}_3$	0.76	27	
	$\text{U}^{4+} + 2\text{H}_2\text{O}(\text{l}) - 4\text{H}^+ - 2\text{e}^- + 2\text{CO}_3^{2-} = \text{UO}_2(\text{CO}_3)_2^{2-}$	7.66	27	
$\text{U}^{4+} + 2\text{H}_2\text{O}(\text{l}) - 4\text{H}^+ - 2\text{e}^- + 3\text{CO}_3^{2-} = \text{UO}_2(\text{CO}_3)_3^{4-}$	12.56	27		

Table 3. Continued

Actinides	Reaction	log $\beta$	Ref.	
<b>Neptunium III</b>	$\text{Np}^{4+} + e^- = \text{Np}^{3+}$	3.70	16	
	$\text{Np}^{4+} + \text{H}_2\text{O}(\text{l}) - \text{H}^+ + e^- = \text{NpOH}^{2+}$	-3.1	16	
	$\text{Np}^{4+} + 3\text{CO}_3^{2-} + e^- = \text{Np}(\text{CO}_3)_3^{3-}$	19.35	16	
<b>IV</b>	$\text{Np}^{4+} + \text{H}_2\text{O}(\text{l}) - \text{H}^+ = \text{NpOH}^{3+}$	0.50	24	
	$\text{Np}^{4+} + 2\text{H}_2\text{O}(\text{l}) - 2\text{H}^+ = \text{Np}(\text{OH})_2^{2+}$	0.31	24	
	$\text{Np}^{4+} + 3\text{H}_2\text{O}(\text{l}) - 3\text{H}^+ = \text{Np}(\text{OH})_3^+$	-2.79	24	
	$\text{Np}^{4+} + 4\text{H}_2\text{O}(\text{l}) - 4\text{H}^+ = \text{Np}(\text{OH})_4^0$	-8.29	24	
	$\text{Np}^{4+} + 3\text{H}_2\text{O}(\text{l}) - 3\text{H}^+ + \text{CO}_3^{2-} = \text{Np}(\text{OH})_3\text{CO}_3^-$	6.03	22	
	$\text{Np}^{4+} + 2\text{H}_2\text{O}(\text{l}) - 2\text{H}^+ + 2\text{CO}_3^{2-} = \text{Np}(\text{OH})_2(\text{CO}_3)_2^{2-}$	16.96	22	
	$\text{Np}^{4+} + 4\text{H}_2\text{O}(\text{l}) - 4\text{H}^+ + \text{CO}_3^{2-} = \text{Np}(\text{OH})_4\text{CO}_3^-$	-4.57	22	
	$\text{Np}^{4+} + 5\text{CO}_3^{2-} = \text{Np}(\text{CO}_3)_5^{6-}$	35.55	16	
	$\text{Np}^{4+} + \text{Cl}^- = \text{NpCl}^{3+}$	1.50	16	
	$\text{Np}^{4+} + \text{SO}_4^{2-} = \text{NpSO}_4^{2+}$	6.85	16	
	$\text{Np}^{4+} + \text{F}^- = \text{NpF}^{3+}$	8.96	16	
	$\text{Np}^{4+} + 2\text{F}^- = \text{NpF}_2^{2+}$	15.70	16	
	<b>V</b>	$\text{Np}^{4+} + 2\text{H}_2\text{O}(\text{l}) - 4\text{H}^+ - e^- = \text{NpO}_2^+$	-10.20	16
		$\text{Np}^{4+} + 3\text{H}_2\text{O}(\text{l}) - 5\text{H}^+ - e^- = \text{NpO}_2\text{OH}^0$	-21.5	16
$\text{Np}^{4+} + 4\text{H}_2\text{O}(\text{l}) - 6\text{H}^+ - e^- = \text{NpO}_2(\text{OH})_2^-$		-33.8	16	
$\text{Np}^{4+} + 2\text{H}_2\text{O}(\text{l}) - 4\text{H}^+ + \text{SO}_4^{2-} - e^- = \text{NpO}_2\text{SO}_4^-$		-9.76	16	
$\text{Np}^{4+} + 2\text{H}_2\text{O}(\text{l}) - 4\text{H}^+ + \text{F}^- - e^- = \text{NpO}_2\text{SO}_4^-$		-9.0	16	
$\text{Np}^{4+} + 2\text{H}_2\text{O}(\text{l}) - 4\text{H}^+ + \text{CO}_3^{2-} - e^- = \text{NpO}_2\text{CO}_3^-$		-5.40	32	
$\text{Np}^{4+} + 2\text{H}_2\text{O}(\text{l}) - 4\text{H}^+ + 2\text{CO}_3^{2-} - e^- = \text{NpO}_2(\text{CO}_3)_2^{3-}$		-3.65	32	
$\text{Np}^{4+} + 2\text{H}_2\text{O}(\text{l}) - 4\text{H}^+ + 3\text{CO}_3^{2-} - e^- = \text{NpO}_2(\text{CO}_3)_3^{5-}$		-4.66	32	
$\text{Np}^{4+} + 3\text{H}_2\text{O}(\text{l}) - 5\text{H}^+ + 2\text{CO}_3^{2-} - e^- = \text{NpO}_2(\text{CO}_3)_2\text{OH}^+$		-15.50	16	
<b>VI</b>		$\text{Np}^{4+} + 2\text{H}_2\text{O}(\text{l}) - 4\text{H}^+ - 2e^- = \text{NpO}_2^{2+}$	-29.8	16
	$\text{Np}^{4+} + 3\text{H}_2\text{O}(\text{l}) - 5\text{H}^+ - 2e^- = \text{NpO}_2\text{OH}^+$	-34.9	16	
	$2\text{Np}^{4+} + 6\text{H}_2\text{O}(\text{l}) - 10\text{H}^+ - 4e^- = (\text{NpO}_2)_2(\text{OH})_2^{2+}$	-65.87	16	
	$\text{Np}^{4+} + 2\text{H}_2\text{O}(\text{l}) - 4\text{H}^+ - 2e^- + \text{CO}_3^{2-} = \text{NpO}_2\text{CO}_3^0$	-20.48	16	
	$\text{Np}^{4+} + 2\text{H}_2\text{O}(\text{l}) - 4\text{H}^+ - 2e^- + 2\text{CO}_3^{2-} = \text{NpO}_2(\text{CO}_3)_2^{2-}$	-13.28	16	
	$3\text{Np}^{4+} + 6\text{H}_2\text{O}(\text{l}) - 12\text{H}^+ - 6e^- + 6\text{CO}_3^{2-} = (\text{NpO}_2)_3(\text{CO}_3)_6^{6-}$	-35.63	16	
<b>Plutonium III</b>	$\text{Pu}^{4+} + e^- = \text{Pu}^{3+}$	17.7	16	
	$\text{Pu}^{4+} + \text{H}_2\text{O}(\text{l}) - \text{H}^+ + e^- = \text{PuOH}^{3+}$	10.8	16	
	$\text{Pu}^{4+} + \text{Cl}^- + e^- = \text{PuCl}^{2+}$	18.90	16	
<b>IV</b>	$\text{Pu}^{4+} + \text{H}_2\text{O}(\text{l}) - \text{H}^+ = \text{PuOH}^{3+}$	0.60	24	
	$\text{Pu}^{4+} + 2\text{H}_2\text{O}(\text{l}) - 2\text{H}^+ = \text{Pu}(\text{OH})_2^{2+}$	0.61	24	
	$\text{Pu}^{4+} + 3\text{H}_2\text{O}(\text{l}) - 3\text{H}^+ = \text{Pu}(\text{OH})_3^+$	-2.30	24	
	$\text{Pu}^{4+} + 4\text{H}_2\text{O}(\text{l}) - 4\text{H}^+ = \text{Pu}(\text{OH})_4^0$	-7.90	24	
	$\text{Pu}^{4+} + \text{SO}_4^{2-} = \text{PuSO}_4^{2+}$	6.9	16	
	$\text{Pu}^{4+} + \text{Cl}^- = \text{PuCl}^{3+}$	1.80	16	
	$\text{Pu}^{4+} + \text{F}^- = \text{PuF}^{3+}$	8.84	16	
	$\text{Pu}^{4+} + \text{CO}_3^{2-} = \text{PuCO}_3^{2+}$	13.60	22	
	$\text{Pu}^{4+} + 2\text{CO}_3^{2-} = \text{Pu}(\text{CO}_3)_2^0$	24.00	22	
	$\text{Pu}^{4+} + 3\text{CO}_3^{2-} = \text{Pu}(\text{CO}_3)_3^{2-}$	31.50	22	
	$\text{Pu}^{4+} + 4\text{CO}_3^{2-} = \text{Pu}(\text{CO}_3)_4^{4-}$	34.50	22	
	$\text{Pu}^{4+} + 5\text{CO}_3^{2-} = \text{Pu}(\text{CO}_3)_5^{6-}$	32.80	22	
	$\text{Pu}^{4+} + 2\text{H}_2\text{O}(\text{l}) - 2\text{H}^+ + 2\text{CO}_3^{2-} = \text{Pu}(\text{OH})_2(\text{CO}_3)_2^{2-}$	18.40	22	
	$\text{Pu}^{4+} + 3\text{H}_2\text{O}(\text{l}) - 3\text{H}^+ + \text{CO}_3^{2-} = \text{Pu}(\text{OH})_3\text{CO}_3^-$	6.00	22	
	$\text{Pu}^{4+} + 4\text{H}_2\text{O}(\text{l}) - 4\text{H}^+ + \text{CO}_3^{2-} = \text{Pu}(\text{OH})_4\text{CO}_3^{2-}$	-4.90	22	
	$\text{Pu}^{4+} + 4\text{H}_2\text{O}(\text{l}) - 4\text{H}^+ + 2\text{CO}_3^{2-} = \text{Pu}(\text{OH})_4(\text{CO}_3)_2^{4-}$	-3.50	22	

Table 3. Continued

Actinides	Reaction	log $\beta$	Ref.
V	$\text{Pu}^{4+} + 2\text{H}_2\text{O(l)} - 4\text{H}^+ - \text{e}^- = \text{PuO}_2^+$	-17.5	16
	$\text{Pu}^{4+} + 2\text{H}_2\text{O(l)} - 4\text{H}^+ + \text{CO}_3^{2-} - \text{e}^- = \text{PuO}_2\text{CO}_3^-$	-12.38	16
	$\text{Pu}^{4+} + 2\text{H}_2\text{O(l)} - 4\text{H}^+ - \text{e}^- + 3\text{CO}_3^{2-} = \text{PuO}_2(\text{CO}_3)_3^{5-}$	-12.48	16
VI	$\text{Pu}^{4+} + 2\text{H}_2\text{O(l)} - 4\text{H}^+ - 2\text{e}^- = \text{PuO}_2^{2+}$	-33.3	16
	$\text{Pu}^{4+} + 3\text{H}_2\text{O(l)} - 5\text{H}^+ - 2\text{e}^- = \text{PuO}_2\text{OH}^+$	-38.8	16
	$\text{Pu}^{4+} + 4\text{H}_2\text{O(l)} - 6\text{H}^+ - 2\text{e}^- = \text{PuO}_2(\text{OH})_2^0$	-46.5	16
	$2\text{Pu}^{4+} + 6\text{H}_2\text{O(l)} - 10\text{H}^+ - 4\text{e}^- = (\text{PuO}_2)_2(\text{OH})_2^{2+}$	-74.1	16
	$\text{Pu}^{4+} + 2\text{H}_2\text{O(l)} - 4\text{H}^+ - 2\text{e}^- + \text{SO}_4^{2-} = \text{PuO}_2\text{SO}_4$	-29.9	16
	$\text{Pu}^{4+} + 2\text{H}_2\text{O(l)} - 4\text{H}^+ - 2\text{e}^- + \text{CO}_3^{2-} = \text{PuO}_2\text{CO}_3$	-23.9	27
	$\text{Pu}^{4+} + 2\text{H}_2\text{O(l)} - 4\text{H}^+ - 2\text{e}^- + 2\text{CO}_3^{2-} = \text{PuO}_2(\text{CO}_3)_2^{2-}$	-18.4	27
	$\text{Pu}^{4+} + 2\text{H}_2\text{O(l)} - 4\text{H}^+ - 2\text{e}^- + 3\text{CO}_3^{2-} = \text{PuO}_2(\text{CO}_3)_3^{4-}$	-15.8	27
	$\text{Pu}^{4+} + 2\text{H}_2\text{O(l)} - 4\text{H}^+ - 2\text{e}^- + \text{Cl}^- = \text{PuO}_2\text{Cl}^+$	-32.6	16
	$\text{Pu}^{4+} + 2\text{H}_2\text{O(l)} - 4\text{H}^+ - 2\text{e}^- + 2\text{Cl}^- = \text{PuO}_2\text{Cl}_2$	-33.9	16
	$\text{Pu}^{4+} + 2\text{H}_2\text{O(l)} - 4\text{H}^+ - 2\text{e}^- + \text{F}^- = \text{PuO}_2\text{F}^+$	-28.74	16
$\text{Pu}^{4+} + 2\text{H}_2\text{O(l)} - 4\text{H}^+ - 2\text{e}^- + 2\text{F}^- = \text{PuO}_2\text{F}_2$	-26.05	16	

Table 4. Solids and their solubility product ( $K_s^0$ ) of actinides used in this study

Actinides	Reaction	log $K_s^0$	Ref.
Am	$\text{Am}^{3+} + 3\text{H}_2\text{O} - 3\text{H}^+ = \text{Am}(\text{OH})_3 \text{ (cr)}$	15.2	15
	$\text{Am}^{3+} + 3\text{H}_2\text{O} - 3\text{H}^+ = \text{Am}(\text{OH})_3 \text{ (am)}$	17.0	15
	$2\text{Am}^{3+} + 3\text{CO}_3^{2-} = \text{Am}_2(\text{CO}_3)_3$	-33.4	21
	$\text{Am}^{3+} + \text{H}_2\text{O} - 2\text{H}^+ + \text{HCO}_3^- = \text{AmOHCO}_3 \text{ (c)}$	1.63	21
	$\text{Am}^{3+} + \text{Na}^+ - 2\text{H}^+ + 2\text{HCO}_3^- = \text{NaAm}(\text{CO}_3)_2$	-0.34	21
Np	$\text{Np}^{4+} + 4\text{H}_2\text{O(l)} - 4\text{H}^+ = \text{Np}(\text{OH})_4 \text{ (am) or NpO}_2 \cdot x\text{H}_2\text{O(am)}$	-0.7	24
	$\text{Np}^{4+} + 2\text{H}_2\text{O(l)} - 4\text{H}^+ = \text{NpO}_2 \text{ (cr)}$	-7.7	24
	$\text{NpO}_2^+ + \text{H}_2\text{O(l)} - \text{H}^+ = \text{NpO}_2\text{OH} \text{ (am, aged)}$	4.6	33
	$\text{NpO}_2^+ + \text{H}_2\text{O(l)} - \text{H}^+ = \text{NpO}_2\text{OH} \text{ (am, fresh)}$	5.2	33
	$\text{NpO}_2^+ - \text{H}^+ + \text{Na}^+ + \text{HCO}_3^- = \text{NaNpO}_2\text{CO}_3 \text{ (s)}$	-0.66	33
	$\text{NpO}_2^+ - 2\text{H}^+ + 3\text{Na}^+ + 2\text{HCO}_3^- = \text{Na}_3\text{NpO}_2(\text{CO}_3)_2 \text{ (s)}$	6.51	33
$2\text{NpO}_2^+ + \text{H}_2\text{O(l)} - 2\text{H}^+ = \text{Np}_2\text{O}_5 \text{ (c)}$	8.0	35	
Pu	$\text{Pu}^{3+} + 3\text{H}_2\text{O} - 3\text{H}^+ = \text{Pu}(\text{OH})_3 \text{ (cr)}$	15.8	16
	$\text{Pu}^{4+} + 4\text{H}_2\text{O} - 4\text{H}^+ = \text{Pu}(\text{OH})_4 \text{ (am)}$	-2.5	24
	$\text{Pu}^{4+} + 2\text{H}_2\text{O} - 4\text{H}^+ = \text{PuO}_2 \text{ (cr)}$	-8.0	24
	$\text{PuO}_2^+ + \text{H}_2\text{O(l)} - \text{H}^+ = \text{PuO}_2\text{OH(am)}$	5.0	16
	$\text{PuO}_2^{2+} + 3\text{H}_2\text{O(l)} - 2\text{H}^+ = \text{PuO}_2(\text{OH})_2 \cdot \text{H}_2\text{O(c)}$	5.5	16
U	$\text{U}^{4+} + 2\text{H}_2\text{O(l)} - 4\text{H}^+ = \text{UO}_2 \text{ (c) (uraninite)}$	-4.9	24
	$\text{U}^{4+} + 4\text{H}_2\text{O(l)} - 4\text{H}^+ = \text{U}(\text{OH})_4 \text{ (am)}$	1.5	24
	$\text{UO}_2^{2+} + 3\text{H}_2\text{O(l)} - 2\text{H}^+ = \text{UO}_3 \text{ (c), } 2\text{H}_2\text{O} \text{ (c) (schocpitc)}$	5.4	28
	$2\text{UO}_2^{2+} + \text{SiO}_2 \text{ (aq)} + 4\text{H}_2\text{O(l)} - 4\text{H}^+ = (\text{UO}_2)_2\text{SiO}_4 \cdot 2\text{H}_2\text{O} \text{ (soddyite)}$	6.2	31
	$\text{UO}_2^{2+} - \text{H}^+ + \text{HCO}_3^- = \text{UO}_2\text{CO}_3 \text{ (rutherfordine)}$	-4.2	29
	$2\text{UO}_2^{2+} + 2\text{Na}^+ + 3\text{H}_2\text{O(l)} - 6\text{H}^+ = \text{Na}_2\text{U}_2\text{O}_7$	26.0	28

mental study were predicted by applying a semi-empirical electrostatic model.

## RESULTS AND DISCUSSION

For the groundwater condition used in the

present study, the aqueous phase speciation of Np, Am, Pu and U was investigated (Figures 1(A) to 1(D)). The concentration of solution measured from the leaching experiments tests was compared with the calculated solubility that was calculated with the assumption of equi-

librium (Figures 2 and 4 to 6).

<Am>

Americium exists solely as a trivalent state in the condition of natural granitic groundwater. Therefore, the speciation and solubility of americium is independent of the value of Eh. However, the carbonate concentration and pH affect significantly the speciation and solubility of Am, as shown in Figure 1(A). It can be seen that the area where the americium carbonate complexes are predominant becomes wider with increasing partial pressure of carbon dioxide and pH. Higher partial pressure of the carbon dioxide, the higher carbonate concentration in solution and leads to stronger formation of the carbonate complexes of americium. The hydroxy complexes of americium are the dominant species in the neutral and alkaline regions at a relatively low partial pressure. The measured pH of the leaching test falls in all the regions where the americium carbonate complexes are predominant. For samples S1 to S3,  $AmCO_3^+$  is the dominating aqueous species, for S4  $Am(CO_3)_2^-$ , and for S4 and S5  $Am(CO_3)_3^{3-}$ .

$AmOHCO_3(cr)$  has been considered as the stable solid phase of americium over a broad pH region. The comparison between the calculated solubility of  $AmOHCO_3(cr)$  and measured concentration is shown in Figure 2. The solubility of  $AmOHCO_3(cr)$  decreases with increasing pH, exhibits a minimum value near pH 8.5, and increases again due to a strong formation of carbonate complexes in the high pH range. The calculated solubilities agree within one order of magnitude with the experimental data after 450nm filtration for samples without iron (S1 to S3). The measured data after 1.8nm-ultrafiltration for S1 to S3 are all much lower than those after 450nm filtration, suggesting strong colloid formation. In the system with iron powder, the measured concentrations for samples S5 and S6 are several orders of magnitude lower than the calculated solubilities. Americium was probably adsorbed onto the corroded iron powder surface. There is

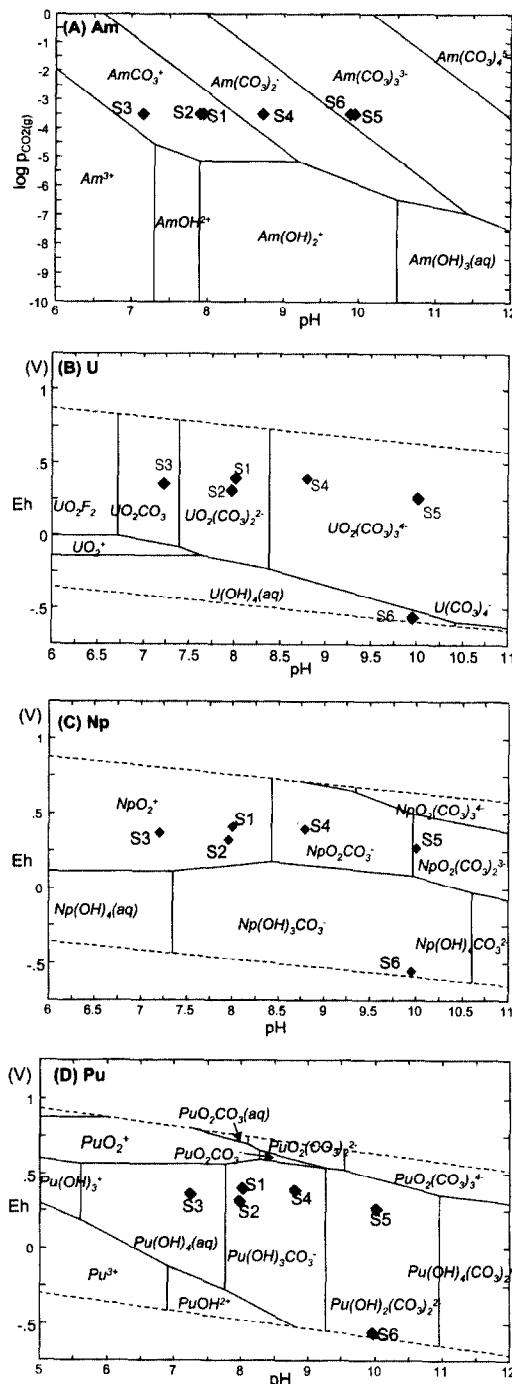


Figure 1. Eh-pH diagram for aqueous species of (A) Am, (B) U, (C) Np, and (D) Np (the diamond-shape symbol corresponds to the measured pH and Eh of samples S1 to S6 each sample; dotted lines represent water stability line ion of pH).

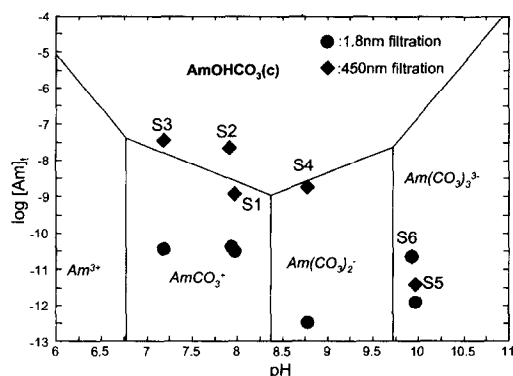


Figure 2. Calculated solubility of  $\text{AmOHCO}_3(\text{s})$  as function of pH and its comparison with the concentration of aqueous phase measured in leaching experiment.

little difference between the concentration after 450nm and 1.8nm filtration of S5 and S6. This indicates that the colloid effect of americium would be insignificant in the system with the addition of iron powder. Presumably, the americium species were more strongly bounded on the iron powder surface sites than colloids.

### <U>

Figure 1(B) is the Eh-pH diagram for the aqueous speciation of uranium. Under oxidizing conditions, the carbonate complexes of U(VI) are predominant in the neutral and alkaline pH regions. The region where the carbonate complexes are predominant enlarges with increasing pH.  $\text{UO}_2^+(\text{aq})$  is the dominant aqueous species under acidic and mildly reducing conditions. Under strongly reducing conditions, the predominant aqueous species is  $\text{U}(\text{OH})_4(\text{aq})$  over a broad pH range, and it is converted into the carbonate complex of U(IV) or U(VI) in a high pH region. For samples S1 to S5, the predominant species seems to be the carbonate complex of U(VI).

In studies on uranium solubility in natural groundwater the tetravalent uraninite has been considered as a representative solubility-limiting solid phase. However, some studies<sup>25,26</sup> showed that the measured solubility of tetravalent actinides,  $\text{AnO}_2(\text{s})$  and  $\text{AnO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ , in a

neutral and alkaline solution would be within the same order, even though the solubility-product of the crystalline tetravalent actinide solids is about 6–7 orders of magnitude lower than that of the respective amorphous hydroxides. Neck and Kim<sup>27</sup> argued that an amorphous surface layer would be formed on the surface of a bulk crystalline dioxide and be equilibrated with radionuclides in the solution. In this study, it was assumed that  $\text{U}(\text{OH})_4(\text{am})$  is the solubility-limiting solid of U(IV) in a neutral or alkaline solution. The same assumption was also applied to the solid of Np(IV) and Pu(IV).

Over a wide range of pH, Eh-conditions, hexavalent soddyite or schoepite can be a stable solid phase of uranium. The content of silicon in groundwater is a critical factor determining which of the two solids phase is more stable (Figure 3). Based on the present thermodynamic data, the critical value of the silicon concentration is equivalent to the difference of the solubility-product of both solids ( $\log [\text{SiO}_2(\text{aq})] = -4.5$ ), and it is independent of pH, carbonate concentration and Eh. When the silicon concentration in the solution is greater than the critical value (as in the studied groundwater), soddyite is the stable solid phase of U(VI), and in the reverse case the schoepite is more stable. Furthermore, in the leaching test under investigation, a secondary phase precipitated, which was identified as a U-silicate by SEM-EDX.<sup>17</sup> In the region where soddyite is stable, the solubility decreases with silicon concentration.

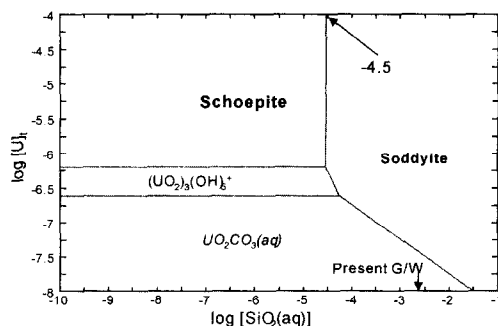


Figure 3. Effect of concentration of  $\text{SiO}_2(\text{aq})$  on formation of U(VI) solids (Eh=0.1V and pH=7).



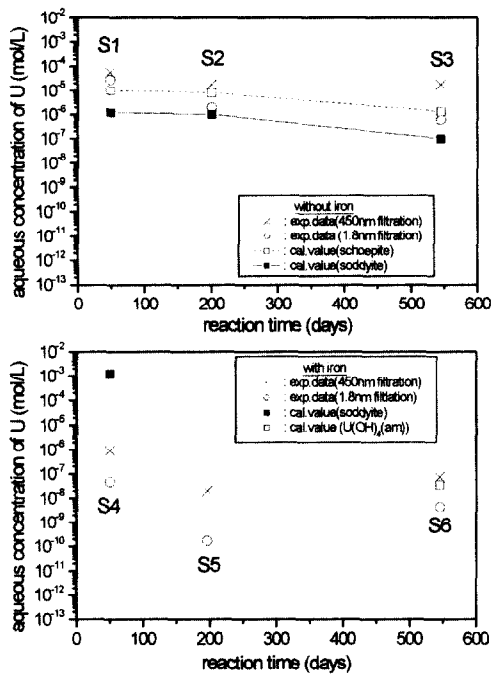


Figure 4. Comparison of calculated solubility with measured concentration of U. (S1, S2 and S3: samples without addition of iron powder; S4, S5 and S6: samples with addition of iron powder)

This is due to the increase of the degree of saturation of the silicon solid phase.

Figure 4 shows the comparison between the measured and calculated concentration of uranium. For samples S1 to S3, the calculated solubilities of soddyite are one or two orders of magnitude less than the measured data. Although the solubility of schoepite represents better the measured data, there is no evidence that the uranium concentration is controlled by the precipitation of schoepite. For sample S4, the calculated solubility is several orders of magnitude higher than what was measured. For the measured condition of S5, the calculated solubility of uranium exceeds the inventory-limit maximum concentration ( $5.5 \times 10^{-2}$  mol/L) in the solution of spent nuclear fuel used in the leaching test. Measured concentrations of S4 and S5 are much lower than the calculated solubilities. This discrepancy is ascribed to the

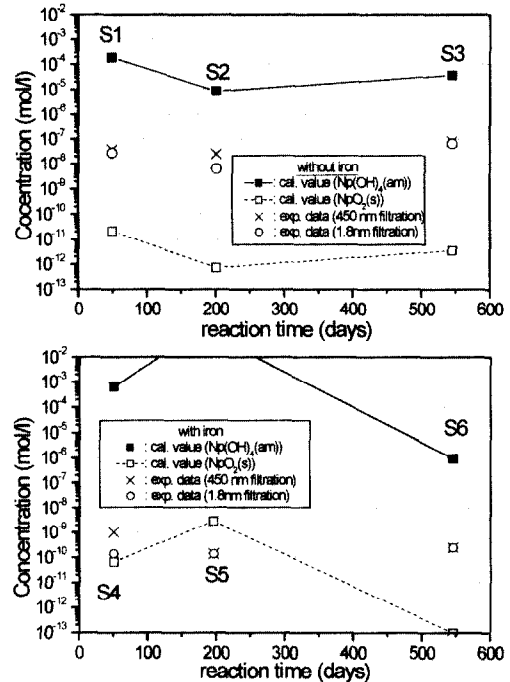


Figure 5. Comparison of calculated solubility with measured concentration of Np. (S1, S2 and S3: samples without addition of iron powder; S4, S5 and S6: samples with addition of iron powder)

adsorption of uranium onto the iron corrosion products or coprecipitation. The measured concentration of S6 is close to the calculated solubility of  $U(OH)_4(am)$ .

### <Np>

Neptunium exists as a pentavalent state under oxidizing conditions and a tetravalent state under reducing conditions (Fig.1 (C)). The predominant aqueous species changes from the hydroxy complexes to the carbonate complexes with increasing pH.  $NpO_2^+$  appears as the dominating species in samples S1 to S3 of the leaching test, and  $NpO_2CO_3^-$ ,  $NpO_2(CO_3)_2^{3-}$ , and  $Np(OH)_3CO_3^-$  in samples S4, S5 and S6, respectively.

Figure 5 shows that the measured concentrations for samples S1 to S3 without iron powder lie between the computed concentrations of  $Np(OH)_4(am)$  and  $NpO_2(s)$ . The solubility of  $Np(OH)_4(am)$  is about two or three orders of

magnitude higher than the measured concentration. For samples with iron powder (S4 to S6), the measured data is much lower than the calculated solubilities of  $\text{Pu}(\text{OH})_4(\text{am})$ . Probably after the release of neptunium from spent fuel, it was adsorbed onto the surfaces of the corroded iron powder.<sup>9)</sup> On the other hand, there is little difference between the measured concentration after 450nm and 1.8nm filtration for both solutions without and with iron powder. This result indicates a little colloid formation of neptunium.

### <Pu>

In groundwater of deep geological formations, the dominant aqueous species of plutonium exists mostly as the trivalent or tetravalent states, as shown in Figure 1(D). With increasing pH, the dominant aqueous species change from the hydroxyl to the carbonate complexes. The area where the aqueous species of  $\text{Pu}(\text{III})$  leading to a high solubility are predominant widens with decreasing pH and Eh. The measured pH and Eh of the leaching test exist in all the regions where the complexes of  $\text{Pu}(\text{IV})$  are the dominating species. For samples S1, S2 and S4,  $\text{Pu}(\text{OH})_3\text{CO}_3^-$  is predominant, for S3  $\text{Pu}(\text{OH})_4(\text{aq})$ , and for S5 and S6  $\text{Pu}(\text{OH})_2(\text{CO}_3)_2^{2-}$ .

$\text{Pu}(\text{OH})_4(\text{am})$  is considered as the most stable solid phase of plutonium over a broad pH and Eh range. At the conditions of samples S1 to S3 without iron powder, the solubility of  $\text{Pu}(\text{OH})_4(\text{am})$  is calculated to about  $1.0 \times 10^{-10}$  mol/L, which is at least three orders of magnitude lower than the measured concentration (Figure 6). Plutonium colloid was formed in the experiment. Moreover, due to radiolytic oxidation  $\text{Pu}(\text{IV})$  was transformed into  $\text{Pu}(\text{V})$  or  $\text{Pu}(\text{VI})$ . In particular  $\text{Pu}(\text{V})$  has a significantly higher solubility than  $\text{Pu}(\text{IV})$ . In the presence of iron powder (solutions S4 to S6), oxidants formed by the radiolysis of the spent fuel may be consumed by the Fe-oxidation. The calculated solubility for S4 exists between the measured concentration after 1.8nm and 450nm filtration.

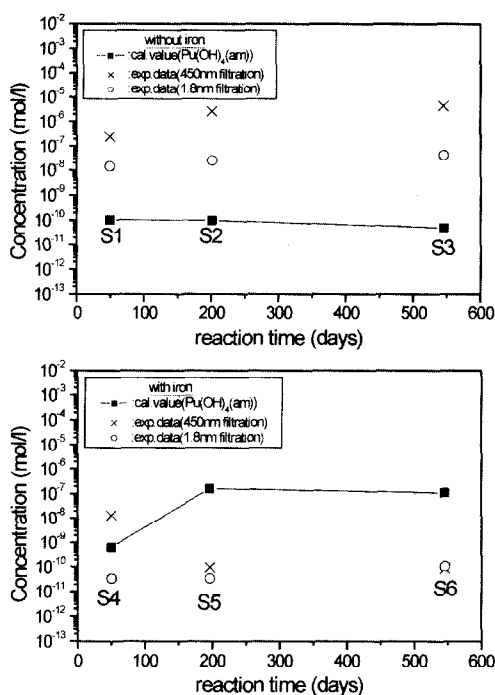


Figure 6. Comparison of calculated solubility with measured concentration of Pu. (S1, S2 and S3: samples without addition of iron powder; S4, S5 and S6: samples with addition of iron powder)

The calculated solubility for S5 and S6 with iron powder is much higher than the measured concentration, indicating a significant adsorption onto the iron surface.

## CONCLUSIONS

The speciation and solubility of Am, U, Np and Pu in granitic groundwater were calculated using geochemical codes with recent thermodynamic data selected from the literature. Calculated solubilities were compared to experimental data from leaching test with spent  $\text{UO}_2$  fuel powder in the respective solution without and with the addition of iron powder under the  $\text{Ar-CO}_2$  atmosphere of 0.03% carbon dioxide gas.

The calculated solubilities of americium and uranium in the solution without iron powder agree well with experimental data, but those of

neptunium and plutonium do not match well with the measured data, due to non-equilibrium effects such as colloid formation or radiolytic oxidation. The measured concentration of actinides in the solution with iron powder is much lower than what was predicted. This is attributed to the adsorption onto the corroded iron surface or co-precipitation. At present, there is a lack of information available for such processes. Additional experiments with well-defined mixed composites in the solution would be needed to better elucidate the formation of secondary mineral, co-precipitation, adsorption of actinide on to corroded iron, although it will be time consuming and very difficult. But no doubt such experiments will be an essential way to improve our understanding of the corrosion and dissolution of spent nuclear fuel as well as to obtain the related thermodynamic data.

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