

COMPARISON BETWEEN EXPERIMENTALLY MEASURED AND THERMODYNAMICALLY CALCULATED SOLUBILITIES OF UO_2 AND ThO_2 IN KURT GROUND WATER

SEUNG SOO KIM*, MIN HOON BAIK, KWANG CHEOL KANG and JONG WON CHOI

Korea Atomic Energy Research Institute

1045 Daedeok-daero, Yuseong-gu, Daejeon, 305-353, Korea

*Corresponding author. E-mail : nsskim@kaeri.re.kr

Received January 5, 2009

Accepted for Publication April 3, 2009

Solubility of a radionuclide is important for defining the release source term of a radioactive waste in the safety and performance assessments of a radioactive waste repository. When the pH and redox potential of the KURT groundwater were changed by an electrical method, the concentrations of uranium and thorium released from $\text{UO}_2(\text{cr})$ and $\text{ThO}_2(\text{cr})$ at alkali pH (8.1 ~ 11.4) and reducing potential ($E_h < -0.2$ V) conditions were less than 10^{-7} mole/L. Unexpectedly, the concentration of tetravalent thorium is slightly higher than that of uranium at pH = 8.1 and $E_h = -0.2$ V conditions, and this difference may be due to the formation of hydroxide-carbonate complex ions. When $\text{UO}_2(\text{s})$ and $\text{UO}_2(\text{am, hyd.})$, and $\text{ThO}_2(\text{s})$ and $\text{Th}(\text{OH})_4(\text{am})$ were assumed as solubility limiting solid phases, the concentrations of uranium and thorium in the KURT groundwater calculated by the PHREEQC code were comparable to the experimental results. The dominating aqueous species of uranium and thorium were presumed as $\text{UO}_2(\text{CO}_3)_3^{4-}$ and $\text{Th}(\text{OH})_3\text{CO}_3^-$ at pH = 8.1 ~ 9.8, and $\text{UO}_2(\text{OH})_3^-$ and $\text{Th}(\text{OH})_4(\text{aq})$ at pH = 11.4.

KEYWORDS : Solubility, Speciation, Uranium, Thorium, Disposal, KURT

1. INTRODUCTION

The safe disposal of high-level radioactive waste (HLW) is a crucial step in the nuclear cycle. One of the most widely accepted options is the construction of underground facilities to accommodate waste packages in a deep geologic formation [1-2]. To appraise the radiological hazards arising from such a disposal repository, the solubility of radionuclides is used as a source term. Most performance assessments for HLW repositories have identified the low solubility of some elements as a key factor contributing to their safety. In such analyses, solubility is represented rather simplistically as a time-independent 'solubility limit'. Solubility is also defined as the maximum equilibrium concentration that can be reached by a specific element in a solution, and this definition refers to true concentrations in a solution and does not consider colloids [3].

Actinides among the radionuclides are of particular interest in the safety assessment of a HLW disposal owing to their radiological toxicity and long half-life. Their solubility and speciation, which mainly depend on the pH (hydrolysis), E_h (oxidation state), temperature and

the concentrations of ligands (e.g., carbonate, phosphate, humic acid, etc.) in groundwater, are important for defining source terms and understanding transport and retardation processes such as sorption and colloid formation in a deep underground repository [4]. The oxidation state of actinide ions is known as the most significant factor for the solubility of actinide solids except for americium and thorium [5]. Bonding affinity of actinides with ligands increases in the order of $5 < 3 \leq 6 < 4$ for the oxidation number of actinides, and the solubilities of most actinides except for plutonium are generally increased with a carbonate concentration under the oxidizing condition [6]. The effect of cation concentrations on actinide solubility meanwhile is generally not severe, because cations do not form strong complexes with actinides [7-8]. For the most common ligands in the environment, the trend for the strength of complex formation with actinides is OH^- , $\text{CO}_3^{2-}(\text{+ HCO}_3^-) > \text{F}^-$, HPO_4^{2-} , $\text{SO}_4^{2-} > \text{Cl}^-$, NO_3^- [9].

The geochemical behavior of uranium has received extensive study due to the importance of uranium as an energy source and a geochronology indicator. During the past 25 years, research in uranium geochemistry and mineralogy has concentrated on issues pertaining to the

disposal of spent nuclear fuel and related nuclear wastes in subsurface geological repositories [10]. UO_2 has a low solubility at a low Eh value in most natural deep groundwaters, while at higher redox potentials hexavalent uranium (U(VI)) species are stabilized and their solubility increases with orders of magnitude. The decomposition of the surrounding water through a radiolysis by the radiation field from a fuel, whose extent depends on the cooling time and the burn-up of a spent fuel, creates a local oxidizing environment close to the fuel surface. The same effect would also occur for Np(IV) and Pu(IV). However, a radiolysis does not in itself change the redox state of a system, since equivalent amounts of oxidizing and reducing species are produced. Under these conditions, a fuel matrix dissolved as U(VI) complexes may subsequently precipitate [11]. Furthermore, uranium ions could be reduced when they contact reducing groundwater in the far-field of a repository or oxygen-exhausted groundwater by the corrosion of a disposal container, although these effects are not yet clearly understood [12]. The extent of dissolution will also be controlled by the ligands present in the groundwater [11].

Redox-stable Th(IV) can be used as an analogue for other tetravalent actinides (An(IV)) in order to avoid experimental complications from possible redox reactions in the case of U(IV), Np(IV) and Pu(IV) [13-14]. A comprehensive investigation of the predominant complexes of tetravalent actinides in the ternary system An(IV)-OH- CO_3 requires variation of the concentrations of the ligands OH^- and CO_3^{2-} over wide ranges.

Generally, the experimental measurement of the solubility and speciation of an actinide in a reducing groundwater with $pH > 7$ is very difficult, as it may take a long time to reach equilibrium between a solid and groundwater and the concentration of dissolved ions is too low to determine the species. Therefore based on the thermodynamic data of nuclides measured by experiments in solutions with relatively simple compositions, several geochemical codes such as PHREEQC, EQ3/6, MINEQL and MUGREM have been developed in order to estimate the solubility of nuclides. In particular, PHREEQC (V.2) can be employed for speciation and saturation-index calculation, as well as batch reaction and one-dimensional transport calculation [7].

In this study, the solubilities of UO_2 and ThO_2 in a domestic granitic ground water were measured experimentally under various conditions and their solubilities and speciations in the same conditions as the experimental solutions were also calculated by PHREEQC (V.2). These results were then compared with each other as well as with results reported in the literature.

2. EXPERIMENT AND CALCULATION

2.1 Nuclear Materials

For the solubility measurement of uranium and

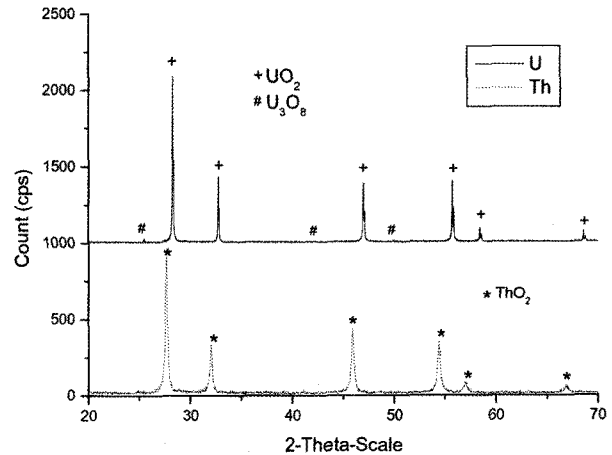


Fig. 1. XRD Patterns of UO_2 and ThO_2 before Washing

Table 1. The Geochemical Conditions of a Natural Granitic Groundwater Obtained from a KURT Borehole

Element	Concentration (mg/L)	Other properties	
Na	17.4	Depth (m)	140~150
K	0.26	Temp (°C)	25.7
Ca	17.3	TDS (mg/L)	246.6
Mg	1.82	DOC (mg/L)	1.23
$CO_3 + HCO_3$	78.4	pH	8.44
Cl	2.18	Conductivity ($\mu S/cm$)	221.4
SO_4	6.97	DO (mg/L)	0.06
F	3.41		
SiO_2	41.3		
Mn	2.2×10^{-2}		
Li	1.7×10^{-2}		
Sr	0.27		
Al	1.6×10^{-2}		
W	1.9×10^{-2}		
Fe	5.0×10^{-2}		
Ba	9.0×10^{-2}		
Mo	3.8×10^{-2}		

thorium in a granitic groundwater, UO_2 and ThO_2 powder were sifted with a 100 mesh sieve and collected. From an X-ray diffraction measurement, a small amount of U_3O_8 in the UO_2 powder was found (Fig. 1), perhaps attributable to oxidation of the powder surface. To remove U_3O_8 from

the surface, the powder was washed with a 0.01M HCl solution for 10 minutes. The powder was then washed with demineralized water and dried in an Ar-filled glove box.

2.2 Groundwater

A natural granitic groundwater was obtained from a borehole in KURT (KAERI Underground Research Tunnel) by using a multi-packer system, at a depth of 140~150 m from the surface, and its composition is shown in Table 1. (Hereafter this groundwater is called the KURT groundwater). Before the sampling of groundwater, the interiors of the connection tubes and an anodized aluminum sampling bottle were flushed with 99.999% nitrogen for more than 10 minutes in order to remove oxygen. The groundwater was stored in the sampling bottle, whose void volume was filled with nitrogen at a slightly higher pressure than atmosphere.

The rock of the KURT is a granitic rock, which has been partly chloritized by past metamorphism. Additionally, plentiful altered and weathered materials such as illite and smectite exist in the fractures and faults in the KURT rock [15].

2.3 Dissolution Experiment

The experiment was performed with 0.1 g of pretreated UO_2 and ThO_2 powders immersed in 400 mL of KURT groundwater in a Teflon reaction vessel (Fig. 2) in an Ar-filled glove box at room temperature. The redox potential (Eh) of the groundwater in the reaction vessel was adjusted to around -0.2, -0.3 and -0.4 V by a potentiometer (Gamry Reference 600). Shown in Fig. 2, working and count electrodes are made of platinum plates having an area of

5 cm², and the count electrode was immersed into groundwater isolated by a Vycor™ membrane glass tube (Corning Incorporated). Redox potential and pH of the groundwater were measured by an ORP combination electrode (Fisher) and a combination pH electrode (Accumet), respectively.

About 20 mL of sample solutions from a reaction vessel were drawn periodically, and the same volume of fresh groundwater was added to maintain a constant volume in the reaction vessel. For simultaneous sampling and filtering of a solution without contact with several mg/L of oxygen in a glove box, a syringe filter with a 0.22 μm pore size (Millex®GP PES) was placed between a needle and a syringe. The needle was injected through a silicon septum in the lid of the reaction vessel (Fig. 2) and supernatant liquid was drawn. The solution was then immediately filtered with an NMWL 500k membrane ultrafilter (3~5 nm pore size, Millipore PM) to remove any colloids that may exist in the solution.

A drop of concentrated nitric acid was added to the sample solutions and the concentrations of uranium and thorium in the solutions were analyzed by an inductively coupled plasma - mass spectrometry (ICP-MS, Perkin-Elmer, Elan 6100).

2.4 Calculation Using PHREEQC

For the calculation of the solubility of a radionuclide, the thermodynamic data of the radionuclide complex, the solubility limiting solid phase (SLSP) of the radionuclide, the composition and temperature of the solution, the activities of the radionuclide aqueous species in equilibrium, etc. are required.

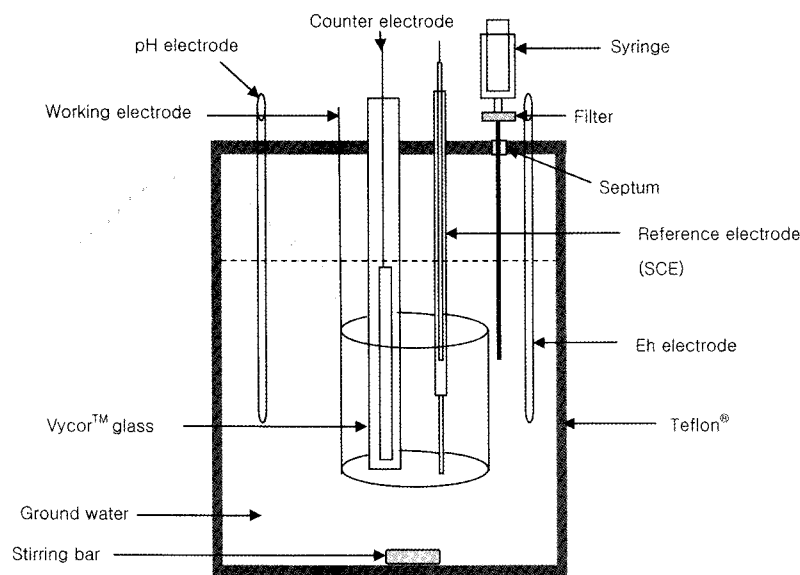


Fig. 2. Schematic Diagram of an Electrochemical Reaction Cell

Thermodynamic data used in this study were obtained from the fifth volume of the series “Chemical Thermodynamics” edited by the OECD/NEA (Nuclear Energy Agency) in 2003 [16], “Chemical Thermodynamic Data Base 01/01” produced by Nagra/PSI [9], and the thermodynamic data used by Keum et al. at KAERI [1]. When the formation constant for the same reaction is different among these thermodynamic data, the OECD/NEA data was accepted.

As the SLSP’s of uranium in a natural groundwater under a reducing condition for a HLW repository, a UO₂ solid has been assumed at SKI, SKB, YJT, PNC and AERE [17]. In general, a UO₂ solid is divided into UO₂(am, hydr.), UO₂(fuel) and uraninite, and UO₂(fuel) corresponds to an intermediate solid between UO₂(am, hydr.) and a well-crystallized uraninite [18]. From a review of thermodynamic calculation results, G. McKinley et al. [19] contended that the uranium concentration limit ranges from 10⁻¹⁰ M (AECL, PNC/H-3) to 10⁻⁶ M (TVO-92). Differences in the uranium concentration limits are governed by the choice of the crystallinity of the uranium dioxide, with the solubility increasing as follows: crystalline < fuel < amorphous.

However, from many recent experimental results, W. Hummel, et al. [9] found that the maximum variation in the solubility of a UO₂ solid is within two orders of magnitude at pH > 4, despite a span of 9 orders of magnitude at pH < 4 according to the degree of crystallinity. This phenomenon was postulated in that the bulk crystalline actinide dioxide (AnO₂(cr)) is covered with an amorphous surface layer by a hydrolysis reaction in the solution, although it was not clearly verified [9, 20]. Therefore, the authors suggested the use of UO₂(s) and ThO₂(s) as new SLSP’s of uranium and thorium, without a distinction between the crystal and amorphous compounds at pH > 6 of solution. These oxides were selected as the SLSP’s for the calculation of the solubilities of uranium and thorium in this study. Additionally, we also considered UO₂(am, hydr.) and Th(OH)₄(am) which have been assumed as the SLSP’s of uranium and thorium in an alkaline solution [21].

From the composition and condition of a groundwater, the thermodynamic data and the SLSP, the dissolved species and the concentrations of uranium and thorium were calculated by PHREEQC (Ver. 2). Change of the composition of the groundwater except for the pH by a change of the Eh value was not corrected in the calculation, although such a change would have occurred.

3. RESULTS AND DISCUSSION

The variations of the concentrations of uranium and thorium in the sample solutions as a function of the dissolution time are shown in Fig. 3. In this figure, the high concentrations of uranium and thorium at an initial dissolution time under pH = 8.1 and Eh = -0.2V condition

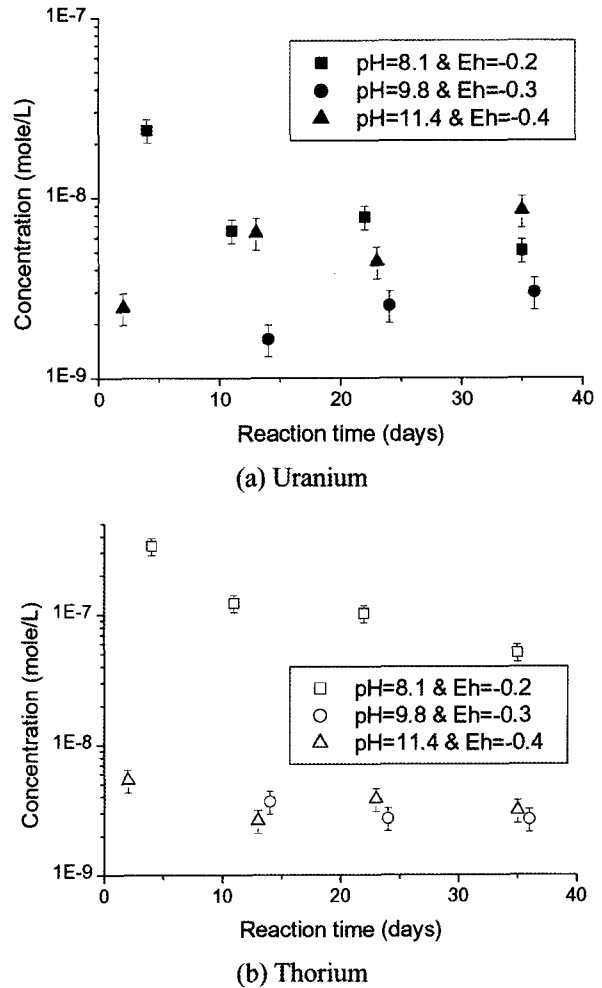


Fig. 3. Variation of the Concentration of (a) Uranium and (b) Thorium at Various pH and Redox Potential (Eh) as a Function of Dissolution Time

may be due to the increase of solubility by the dissolution of oxygen in the glove box at the beginning of an experiment.

The solubility and species of the uranium and thorium in the same experimental solution conditions were calculated by PHREEQC and the results are shown in Table 2.

3.1 Uranium

The pH of the groundwater added with UO₂ and ThO₂ powder was varied from 8.1 to around 11.4 when its redox potential was changed from -0.2 to -0.4 V by a potentiometer. As shown in Fig. 3, the concentration of uranium released from UO₂ remained between 1 × 10⁻⁸ ~ 1 × 10⁻⁹ mole/L in the KURT groundwater at a range of pH 8.1 ~ 11.4 and below a reducing condition of -0.2 V for a dissolution time between 30 ~ 40 days while the concentration may increase slightly at pH=11.4. These

Table 2. The Concentration and Dominant Species of Uranium and Thorium Compounds in KURT Groundwater Calculated by the PHREEQC (V.2) Code

SLSP	pH	Eh (V)	Concentration (mole/L)	Dominant Species	(%)
UO ₂ (s) [UO ₂ (am, hyd)]	8.1	-0.2	7.8 × 10 ^{-10a}	UO ₂ (CO ₃) ₃ ⁴⁻	57
			(7.8 × 10 ⁻⁸ ~ 7.8 × 10 ⁻¹²) ^b	UO ₂ (CO ₃) ₂ ²⁻	27
			[2.4 × 10 ⁻⁸] ^c	U(OH) ₄	13
UO ₂ (s) [UO ₂ (am, hyd)]	9.8	-0.3	4.0 × 10 ^{-9a}	UO ₂ (CO ₃) ₃ ⁴⁻	90
			(4.0 × 10 ⁻⁷ ~ 4.0 × 10 ⁻¹¹) ^b		
UO ₂ (s) [UO ₂ (am, hyd)]	11.4	-0.4	7.1 × 10 ^{-9a}	UO ₂ (OH) ₅ ⁻	85
			(7.1 × 10 ⁻⁷ ~ 7.1 × 10 ⁻¹¹) ^b		
			[2.3 × 10 ⁻⁷] ^c		
ThO ₂ (s) [Th(OH) ₄ (am)]	8.1	-0.2	1.9 × 10 ^{-7d}	Th(OH) ₃ CO ₃ ⁻	72
			(1.2 × 10 ⁻⁶ ~ 3.0 × 10 ⁻⁸) ^e	Th(OH) ₄	14
			[2.3 × 10 ⁻⁸] ^f	Th(OH) ₂ (CO ₃) ₂ ²⁻	13
ThO ₂ (s) [Th(OH) ₄ (am)]	9.8	-0.3	1.0 × 10 ^{-7d}	Th(OH) ₃ CO ₃ ⁻	69
			(6.3 × 10 ⁻⁷ ~ 1.6 × 10 ⁻⁸) ^e	Th(OH) ₄	24
ThO ₂ (s) [Th(OH) ₄ (am)]	11.4	-0.4	[1.3 × 10 ⁻⁸] ^f	Th(OH) ₂ (CO ₃) ₂ ²⁻	7
			3.3 × 10 ^{-8d}	Th(OH) ₄	76
			(1.9 × 10 ⁻⁷ ~ 9.0 × 10 ⁻⁹) ^e	Th(OH) ₃ CO ₃ ⁻	17
			[4.1 × 10 ⁻⁹] ^f	Th(OH) ₄ CO ₃ ²⁻	7

^a Central values of uranium concentration calculated from UO₂(s) as SLSP

^b Whole ranges of uranium concentration calculated from UO₂(s) as SLSP

^c Uranium concentration calculated from UO₂(am, hyd) as SLSP

^d Central values of thorium concentration calculated from ThO₂(s) as SLSP

^e Whole ranges of thorium concentration calculated from ThO₂(s) as SLSP

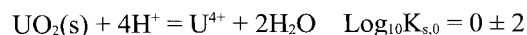
^f Thorium concentration calculated from Th(OH)₄(am) as SLSP

results are similar to the uranium concentration measured from a dissolution experiment with a spent fuel in a groundwater under an atmosphere of 99.7% Ar and 0.03% CO₂(g) [22] and in a synthetic granitic groundwater at pH=9.6 under an anaerobic condition. [11] Rai et al. also reported a similar solubility value of U(IV) in a solution with a range of pH = 8~10 [23].

A study of hydrochemical data from the Canadian URL (Underground Rock Laboratory) is also relevant. Although detailed uranium mineralogy was not reported, a clear trend of decreasing uranium concentration with increasing depth and greater reducing conditions strongly indicated precipitation of the phases, which reduces the aqueous uranium concentration to 10⁻¹⁰ ~ 10⁻⁹ mole/L [3]. Even when pitchblende (U₃O₈) was assumed as a solubility control solid in the thermodynamic modeling, the uranium concentration in a wide range of ground water in contact with pitchblende was less than 10⁻⁷ mole/L [3].

W. Hummel, et al. [9] recommended a rough solubility

product for UO₂(s) with an increased uncertainty range from the large variations in reported solubility products at pH > 6 as follows:



In this calculation, U(OH)₅⁻ was found to be a major soluble ion in the groundwater for UO₂(am, hyd.) when an equilibrium constant (log₁₀K = -16.54) estimated by Grenthe et al. [24] was used for the following reaction: U⁴⁺ + 5H₂O = U(OH)₅⁻ + 5H⁺. However, the thermodynamic datum for the formation of U(OH)₅⁻ was excluded from the solubility calculation of uranium in this study, because U(OH)₅⁻ has not been observed experimentally in a solution below pH 12 [9,17,25]. Nagra/PSI also eliminated the species from their database [9].

From the calculation of the uranium solubility in

KURT groundwater with pH = 8.1 and Eh = -0.2, pH = 9.8 and Eh = -0.3, and pH = 11.4 and Eh = -0.4V, the uranium concentrations were obtained as $7.8 \times 10^{-12} \sim 7.1 \times 10^{-7}$ (central values are $7.8 \times 10^{-10} \sim 7.1 \times 10^{-9}$) and $2.4 \times 10^{-8} \sim 2.3 \times 10^{-7}$ mole/L for UO₂(s) and UO₂(am, hyd.), respectively. When these results are compared with our experimental values (Fig. 3) and a central concentration range is considered for UO₂(s), the uranium concentrations for UO₂(s) show a somewhat better coincidence than those for UO₂(am, hyd.). From our results and experimental results reported in the literature, and the calculated result by PHREEQC, the uranium concentration released from UO₂(cr) in the KURT groundwater is expected to be less than 1×10^{-7} mole/L under a reducing condition, although 8×10^{-7} mole/L may be assigned as a conservative value. However, the calculated solubility of UO₂(am, hyd.) in a domestic groundwater (pH=9.92, Eh=-0.194V) sampled from borehole YS-01 was as high as 2.2×10^{-5} mole/L [2]. This might be due to the higher pH in YS-01 groundwater. Uranium solubility calculated by MUGREM code at Eh = -0.2V was also greatly increased between pH = 7.0 and 9.6 [4]; 3.7×10^9 , 8.4×10^7 , 1.3×10^{-5} and 3.2×10^{-5} mole/L at pH = 7.0, 8.9, 9.1 and 9.6, respectively, even though it did not greatly vary at Eh \leq -0.3V [4].

Dominating dissolved ions were calculated as UO₂(CO₃)₃⁴⁻ at pH = 8.1 ~ 9.8, and UO₂(OH)₃⁻ at pH = 11.4, which are somewhat in agreement with Keum's results; UO₂(CO₃)₃⁴⁻ and UO₂(CO₃)₂²⁻ are major species at $7.5 < \text{pH} < 9.5$, and UO₂(OH)₃⁻ is a major species at pH > 9.5 [1].

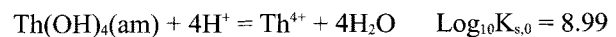
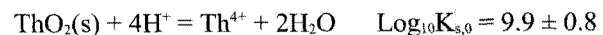
3.2 Thorium

As shown in Fig. 3, the concentration of the thorium released from ThO₂ remained between $10^{-7} \sim 10^{-9}$ mole/L in the KURT groundwater at a range of pH 8.1 ~ 11.4 under a reducing condition. Unexpectedly, the concentration of thorium is slightly higher than that of uranium at the pH=8.1 and Eh=-0.2V conditions. These thorium concentrations are also about 2 orders higher than McKinley's result ($10^{-10} \sim 10^{-9}$ mole/L) calculated by a geochemical code [19]. McKinley did not consider the thorium-hydroxide-carbonate complexes, Th(OH)_y(CO₃)_z^{y-2z}, which have recently been found to be predominant aqueous thorium species under many natural conditions while the complexes are negligible or of minor importance for trivalent and hexavalent actinides such as Am(III), U(VI) and Pu(VI) [13].

Carbonate ions raise the thorium solubility. In Altmaier's solubility experiment [13] with Th(IV) oxyhydroxide and dried ThO₂·xH₂O(am), the concentration of the thorium was increased by about 5 orders of magnitude when the carbonate concentration in the solution was changed from 0 to 0.1M at pH 8 ~ 10. However, Altmaier [13] found a significant reduction of the thorium concentration from 10^{-3} to 10^{-6} mole/L by a decrease of the carbonate concentration from 0.1 to 0.015 M, and Nagra/PSI [9]

reported the solubility of thorium as $10^{-8} \sim 10^{-9}$ mole/L at pH > 7 in the carbonate-free solutions. When the above two results are taken into consideration, our experimental result ($\sim 5 \times 10^{-8}$ mole/L at pH = 8.1 and Eh = -0.2V) at 1.3 mM of carbonate concentration in the KURT groundwater is comparable. The carbonate effect on the solubility of thorium could be decreased in a strong alkaline solution, as shown by the results obtained under pH = 11.4 and Eh = -0.4V in this study. This phenomenon was also found for another tetravalent actinide, Np(IV) [16].

The reactions and solubility product data of ThO₂(s) and Th(OH)₄(am) selected in this study for the calculation of the thorium solubility and speciation are as follows:



The thorium concentrations calculated from ThO₂(s) and Th(OH)₄(am) in the KURT groundwater at pH = 8.1 ~ 11.4 and Eh < -0.2 V are $9.0 \times 10^{-9} \sim 1.2 \times 10^{-6}$ (central values are $3.3 \times 10^{-8} \sim 1.9 \times 10^{-7}$) and $4.1 \times 10^{-9} \sim 2.3 \times 10^{-8}$ mole/L, respectively (Table 2). Compared with our experimental results, the central value of the thorium concentration for ThO₂(s) and the thorium concentration for Th(OH)₄(am) somewhat coincide at pH=8.1 and Eh=-0.2V, and at pH=11.4 and Eh=-0.4, respectively.

From our experimental results (Fig. 3) and central values calculated by a geochemical code (Table 2), the thorium concentration released from ThO₂(cr) in the KURT groundwater is suggested to be less than 2×10^{-7} mole/L at below Eh = -0.2V, although 1.2×10^{-6} mole/L may be assigned as a conservative value.

The dominant aqueous species were calculated as Th(OH)₃CO₃⁻ at pH = 8.1 ~ 9.8 and Eh=-0.2V, and Th(OH)₄(aq) at pH = 11.4 and Eh=-0.4V. Our results for a low concentration and the species of thorium at pH = 11.4 are coincident with results available in the literature [5,13], where the solubility of the measured thorium was very close to that in carbonate-free solutions and Th(OH)₄(aq) was identified in a solution with pH > 11. However, the dominant dissolved ion Th(OH)₃CO₃⁻ at pH = 8.1 ~ 9.8 in this study is different from Th(OH)(CO₃)₄⁵⁻ and Th(OH)₂(CO₃)₂²⁻ found by M. Altmaier, et al. This discrepancy may be attributed to the variation in groundwater compositions.

4. CONCLUSIONS

To understand the behaviors of spent fuel disposed in a deep underground granitic rock, the concentrations of uranium and thorium released from UO₂(cr) and ThO₂(cr) into the KURT groundwater under reducing conditions

were measured. From this experiment, the concentrations of uranium and thorium remained between $10^{-7} \sim 10^{-9}$ mole/L at pH 8.1 ~ 11.4 and Eh < -0.2V, which are comparable to experimental results reported in the literature. The concentration of the redox-stable tetravalent thorium is slightly higher than that of uranium at pH = 8.1 and Eh = -0.2V. This difference may be due to the contribution of the predominant An(IV)-hydroxide-carbonate complex ions, which are negligible or of minor importance in hexavalent actinides such as U(VI). However, the carbonate effect on the solubility of thorium decreased in a strong alkaline solution.

When the central values for UO₂(s) and ThO₂(s) are selected, the concentrations of uranium and thorium calculated by PHREEQC for UO₂(s) and UO₂(am, hyd.), and ThO₂(s) and Th(OH)₄(am) as SLSP's in the same experimental solution conditions were $2.3 \times 10^{-7} \sim 7.8 \times 10^{-10}$ mole/L. This range is not greatly different from the experimental results. Carbonate or hydroxyl carbonate complexes at pH = 8.1 ~ 9.8 and hydroxyl complexes at pH = 11.4 were found to be the dominant aqueous species.

ACKNOWLEDGMENTS

This study was performed as a part of the Mid- and Long-term Nuclear R&D Programs funded by the Ministry of Education, Science and Technology of Korea.

REFERENCES

- [1] D. K. Keum, M. H. Baik and P. S. Hahn, "Speciation and Solubility of Major Actinides under the Deep Groundwater Conditions of Korea," *J. Korean Nuclear Society*, **43**(5), 517 (2002).
- [2] M. H. Baik, S. Y. Lee, J. K. Lee, S. S. Kim, C. K. Park and J. W. Choi, "Review and Compilation of Data on Radionuclides Migration and Retardation for the Performance Assessment of a HLW Repository in Korea," *Nucl. Eng. Technol.*, **40**(7), 593 (2008).
- [3] I. G. McKinley, W. R. Alexander, A. Gautschil and N. Waber, "An Approach to Validation of Solubility Databases for Performance Assessment," *Radiochim. Acta*, **82**, 407 (1998).
- [4] KAERI, Progress Report on the R&D Program for the Disposal of HLW in Korea: Appendix; Korea Atomic Energy Research Institute: Daejeon, Korea (2002).
- [5] G. R. Choppin, "Actinide Speciation in Aquatic Systems," *Marine Chemistry*, **99**, 83 (2006).
- [6] IAEA, "Geochemistry of Long-Lived Transuranic Actinides and Fission Products," IAEA-TECDOC-637, International Atomic Energy Agency (1992).
- [7] D. L. Parkhurst and C. A. J. Appelo, "User's Guide to PHREEQC (Version 2) - A Computer Program for Speciation, Batch-Reaction, One-Dimensional Transport and Inverse Geochemical Calculations," Water-Resources Investigations Report 99-4259, Water Resources of the United States (1999).
- [8] OCRWM, "Dissolved Concentration Limits of Radioactive Elements," ANL-WIS-MD-000010 REV 02, Office of Civilian Radioactive Waste Management (2003).
- [9] W. Hummel, U. Berner, E. Curti, F. J. Pearson and T. Thoenen, *Nagra/PSI Chemical Thermodynamic data base 01/01*, Universal Publishers, Florida, USA (2002).
- [10] K. M. Knupka and R. J. Serne, "Geochemical Factors Affecting the Behavior of Antimony, Cobalt, Europium, Technetium, and Uranium in Vadose Sediments," PNNL-14126, Pacific Northwest National Laboratory (2002).
- [11] L. O. Werme and K. Spahiu, "Direct Disposal of Spent Fuel: Comparison Between Experimental and Modeled Actinide Solubilities in Natural Waters," *J. Alloys and Compounds*, **271**, 194 (1998).
- [12] Sergei Butorin, Kaija Ollila and Yngve Albinsson, "Reduction of Uranyl Carbonate and Hydroxyl Complexes and Neptunyl Carbonate Complexes Studied with Chemical-Electrochemical Methods and RIXS Spectroscopy," POSIVA 2004-01, Posiva, Finland (2004).
- [13] M. Altmaier, V. Neck, R. Muller and Th. Fanghanel, "Solubility of ThO₂.xH₂O(am) in Carbonate Solution and the Formation of Ternary Th(IV) Hydroxide-Carbonate Complexes," *Radiochim. Acta*, **93**, 83 (2005).
- [14] B. Wierczynski, S. Helfer, M. Ochs and G. Skarnemark, "Solubility Measurements and Sorption Studies of Thorium in Cement Pore Water," *J. Alloy and Compounds*, **271**, 272 (1998).
- [15] S. Y. Lee, M. H. Baik and W. J. Cho, "A Study on the Mineralogical and Geochemical Properties of Rocks and Fractures/Faults in KURF," KAERI/TR-3140/2006, Korea Atomic Energy Research Institute (2006).
- [16] F. J. Mompean, M. Illemassene, C. Domenech-Orti and K. B. Said, *Chemical Thermodynamics 5: Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium*, Elsevier, OECD-NEA, Orsay, France (2003).
- [17] S. Takeda, S. Shima, H. Kimura and H. Matsuzuru, "The Aqueous Solubility and Speciation Analysis for Uranium, Neptunium and Selenium by the Geochemical Code (EQ3/6)," JAERI Research 95-069, Japan Atomic Energy Research Institute (1995).
- [18] I. Puigdomenech and J. Bruno, "Modeling Uranium Solubilities in Aqueous Solutions: Validation of a Thermodynamic Data Base for the EQ3/6 Geochemical Codes," SKB-TR-88-21, Swedish Nuclear Fuel and Waste Management Co (1988).
- [19] I. G. McKinley and D. Savage, "Comparison of Solubility Database Used for HLW Performance Assessment," *J. Contaminant Hydrology*, **21**, 335 (1996).
- [20] V. Neck and J. I. Kim, "Solubility and Hydrolysis of Tetravalent Actinides," *Radiochim. Acta*, **89**, 1 (2001).
- [21] W. Runde, S. D. Conradson, D. W. Efurud, N. P. Lu, C. E. vanPelt and C. D. Tait, "Solubility and Sorption of Redox-Sensitive Radionuclides (Np, Pu) in J-13 Water from the Yucca Mountain Site: Comparison Between Experiment and Theory," *Applied Geochemistry*, **17**(7), 837 (2002).
- [22] B. Grambow, A. Loida, A. M. Esparza, P. D. Arocas, J. de Pablo, J. L. Paul, G. Marx, J. P. Glatz, K. Lemmens, K. Ollila and H. Christensen, "Long-Term Safety of Radioactive Waste Disposal: Source Term for Performance Assessment of Spent Fuel as a Waste Form. Final Report," FZKA-6420, Forschungszentrum Karlsruhe, Germany (2000).
- [23] D. Rai, A. Felmy and J. Ryan, "Uranium(IV) Hydrolysis Constant and Solubility Product of UO₂.H₂O(am)," *Inorg. Chem.*, **29**, 7852 (1990).
- [24] I. Grenthe, J. Fuger, R. J. M. Konings, R. J. Lemire, A. B.

Muller, C. Nguyen-Trung and H. Wanner, *Chemical Thermodynamics of Uranium*, Elsevier, Amsterdam, Netherlands (1992).

[25] M. Chandratillake, D. P. Trivedi, M. G. Randall, P. N.

Humphreys and E. J. Kelly, "Criteria for Compilation of a Site-Specific Thermodynamic Database for Geochemical Speciation Calculations," *J. Alloys and Compounds*, **271**, 821 (1998).