

〈**Technical Note**〉

**Effect of pH, Redox Potential (Eh) and Carbonate
Concentration on Actinides Solubility in a
Deep Groundwater of Korea**

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Abstract

KAERI (Korea Atomic Energy Research Institute) is at present preparing a preliminary performance assessment to set up the HLW disposal concept of Korea. The solubility of the radionuclides contained in HLW is necessary as a source term in order to predict their potential migration in both the near and far fields.

The solubility of actinides (Th, Am, U, Np and Pu) for a reference deep groundwater of Korea has been calculated using a geochemical code with thermodynamic data selected by a peer review of existing thermodynamic databases and literature. The solubilities from the experimental study and/or field observations from natural analogue studies are compared. The sensitivity of solubility to the variability of three main parameters of groundwater (pH, Eh, and carbonate concentration) is also investigated.

The results of the sensitivity analysis show that the solubility of actinides strongly depends on the parameters considered. Within the range of parameter values studied (pH=7 to 10, Eh=-0.4 to -0.1V, and carbonate concentration=1.E-5 to 1.E-2 mol/L), the solubility of each actinide exists between 1.4E-10 and 1.6E-6 mol/L for Am, 4.9E-9 and 2.8E-6 mol/L for Th, 3.2E-9 and 5.7E-4 mol/L for U, 1.1E-9 and 1.0E-7 mol/L for Np, and 4.0E-11 and 2.8E-6 mol/L for Pu, respectively.

Key Words : solubility, pH, Eh, carbonate, Th, Am, U, Np, Pu

1. Introduction

Korea Atomic Energy Research Institute (KAERI) is preparing a preliminary performance assessment to set up the HLW disposal concept of Korea. The performance assessment uses the

solubility of radionuclides contained in HLW as source term to estimate radionuclide migration from the repository to the biosphere. In a previous study, we presented the calculated solubility of major actinides for the conditions of four deep groundwaters sampled from two

domestic local sites [1]. The solubility of actinides is known to be strongly dependent on the composition of groundwater, particularly pH, Eh, and carbonate concentration. However, these parameters vary along the flow path of groundwater and are always exposed to analytical error in measurement. It is, therefore, necessary that the sensitivity of actinides solubility to these parameter values be investigated in order to minimize the uncertainty involved.

In this study we have calculated the solubilities of Th, Am, U, Np, and Pu solid phases in a reference deep groundwater of Korea and studied the uncertainty of the solubility with the variation of pH, Eh, and carbonate concentration, within the range of the parameter values found typically in natural granitic groundwater.

2. Calculations

Calculations have been carried out using a geochemical code MUGREM developed by KAERI, Which can deal simultaneously with a multi-geochemical equilibrium reaction system including aqueous complexation reactions, precipitation-dissolution reactions, as well as adsorption reactions [2]. The code was verified through a comparison of calculation results with those obtained from other existing codes such as EQ3/6 and MINTEQA2 [2,3].

The reference groundwater composition used in this study is given in Table 1. The groundwater was sampled using a multipacker system from Yuseong research site, which is located in the Mid-West area of South Korea. The thermodynamic data used in the calculation are from a previous work [1]. Most of the data came from the OECD/NEA thermodynamic data series [4~6] and some data were selected from the literature.

In order to establish the uncertainty range of

Table 1. Reference Groundwater Composition Used in the Study

Species	Composition (mol/L)
Na ⁺	1.55E-3
K ⁺	7.67E-6
Ca ⁺⁺	6.74E-5
Mg ⁺⁺	2.06E-6
SiO ₂	3.08E-4
Cl ⁻	1.18E-4
[CO ₃ ²⁻] _T	4.09E-4
SO ₄ ²⁻	2.40E-5
F	6.68E-4
TDS (mg/L)	101.3
pH	9.9
Eh (mV)	-194
depth (m)	458

actinides solubility with respect to Eh, pH, and carbonate concentration of groundwater, we have treated each parameter an independent variable by varying one of the parameters while keeping the other parameters fixed for each run. The parameter values have been varied within the ranges found in typical granitic groundwater (pH=7 to 10, Eh=-0.4V to -0.1V, and total carbonate content=1.E-5 to 1.E-2 mol/L). In preliminary calculation results, no formation of calcite and magnetite was revealed. This indicates that the concentration of calcium and magnesium in the reference groundwater would be not high enough to form these precipitates, and therefore pH does not constrain the total carbonate concentration in solution.

3. Results and Discussion

Table 2 shows the calculated solubility of actinides for the present groundwater, and their maximum and minimum solubility that can be obtained within the range of parameter values studied. Figures 1 to 5 show the dependence of the solubility with pH, Eh, and total carbonate

Table 2. Solubility, Solubility-limiting Solid Phase and Major Aqueous Species of Actinides for Reference Groundwater

R/N	Solubility (mol/L)	Solubility limiting solid phase	Major aqueous species	Maximum/Minimum
Am	4.3E-10	AmOHCO ₃ (s)	Am(CO ₃) ₂ ⁻ (59%), Am(OH) ₂ ⁺ (26%)	1.6E-6/ 1.4E-10
Th	8.4E-8	Th(OH) ₄ (am)	Th(OH) ₃ CO ₃ ⁻ (96%)	2.8E-6 4.9E-9
U	1.5E-4	U(OH) ₄ (am)	(UO ₂) ₃ (OH) ₇ ⁻ (55%), UO ₂ (OH) ₃ ⁻ (25%), UO ₂ (CO ₃) ₃ ⁴⁻ (18%)	5.7E-4/ 3.2E-9
Np	4.4E-9	Np(OH) ₄ (am)	Np(OH) ₃ CO ₃ ⁻ (63%), Np(OH) ₄ (aq) (23%)	1.0E-7/ 1.1E-9
Pu	8.6E-11	Pu(OH) ₄ (am)	Pu(OH) ₃ CO ₃ ⁻ (47%), Pu(OH) ₄ (aq) (45%)	2.8E-6/ 4.0E-11

* The last column shows the maximum and minimum solubility of each actinide that can be obtained within the range of parameter values studied.

concentration.

3.1. Americium

AmOHCO₃(s) is the predominant solubility-limiting-solid phase of americium in granitic groundwater. However, at high pH and low carbonate content, Am(OH)₃(s) can also be a solubility-limiting-solid phase. The calculated solubility is about three orders of magnitude higher

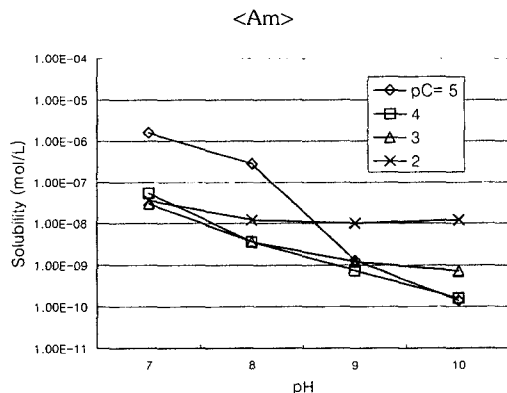


Fig. 1. Solubility of Am as a Function of pH and Total Carbonate Content

than the result by Bruno et al. [7], while it is in the range of the measured americium concentrations in spent fuel dissolution experiments [8~14].

The effect of pH and carbonate concentration on the solubility of americium is given in Figure 1. The solubilities exist between 1.4E-10 and 1.6E-6 mol/L. The pH causes a large variation of solubility at the condition of low carbonate concentration (pC=5 or 4), where the predominant aqueous species changes in the order of AmOH²⁺, AmCO₃⁺ and Am(CO₃)₂⁻, and Am(OH)₂⁺ and Am(OH)₃ with increasing pH. The highest and lowest solubility is obtained at pH 7 and 10 when pC=5, respectively. This is ascribed to the predominance of hydroxo complexes in the both pH values. At a relatively high carbonate concentration (pC=2), pH does not have a significant effect on solubility due to the stabilization of carbonate complexes in solution.

3.2. Thorium

The solid phase, Th(OH)₄(am), is the dominant

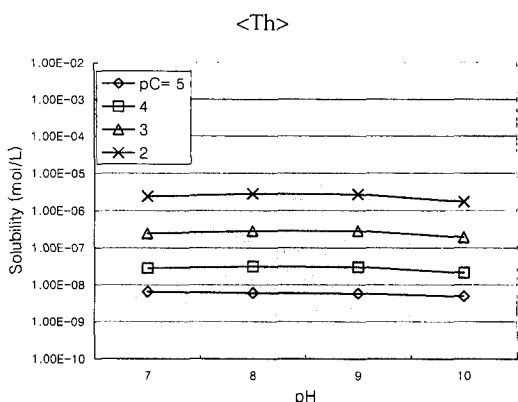


Fig. 2. The Concept of a Safety Function Failure

precipitated compound of thorium in granitic groundwater [15]. The calculated solubility of $\text{Th}(\text{OH})_4(\text{am})$ is one to three orders of magnitude higher than that reported in natural analogue studies ($1.5\text{E-}9$ mol/L in Cigar Lake, Canada [16], $1.75\text{E-}11$ mol/L in El Berrocal [17], and $6\text{E-}11$ to $1.4\text{E-}10$ mol/L in Pocos de Caldas [18]).

In Figure 2 the calculated solubility of $\text{Th}(\text{OH})_4(\text{am})$ is shown as a function of pH and carbonate concentration. The solubility exists between $4.9\text{E-}9$ and $2.8\text{E-}6$ mol/L. The solubility of $\text{Th}(\text{OH})_4(\text{am})$ is almost independent of pH. The highest solubility is obtained at the highest carbonate concentration ($\text{pC}=2$) due to the predominance of $\text{Th}(\text{OH})_3\text{CO}_3$ in solution.

3.3. Uranium

The solubility limiting solid phase of uranium varies with groundwater conditions [1]. Within the range of parameter values studied, $\text{U}(\text{OH})_4(\text{am})$ and $(\text{UO}_2)_2\text{SiO}_4 \cdot 2\text{H}_2\text{O}$ (soddyite) appear to be a stable solid phase of IV and VI valances, respectively. However, schoepite (VI valances) is a stable solid when the silicon concentration in groundwater is less than $10^{-4.5}$, which is the difference of solubility product (K_{sp}) between schoepite and soddyite. The calculated solubility

for the present groundwater is in good agreement with the uranium concentrations observed in natural analogue studies [16~18] and the result by Bruno et al. [7]. However, it is about two orders of magnitude lower than that obtained from spent fuel dissolution tests in granite groundwaters [8].

According to the sensitivity analysis (Figure 3), the calculated solubility of uranium shows a large variation between $3.2\text{E-}9$ and $5.7\text{E-}4$ mol/L. In the result the solubility for the case what $\text{pC}=2$ and $\text{Eh}=-0.1\text{V}$ or -0.2V was omitted because of the absence of formation of stable solid phases. The highest solubility is obtained when $\text{pH}=10$,

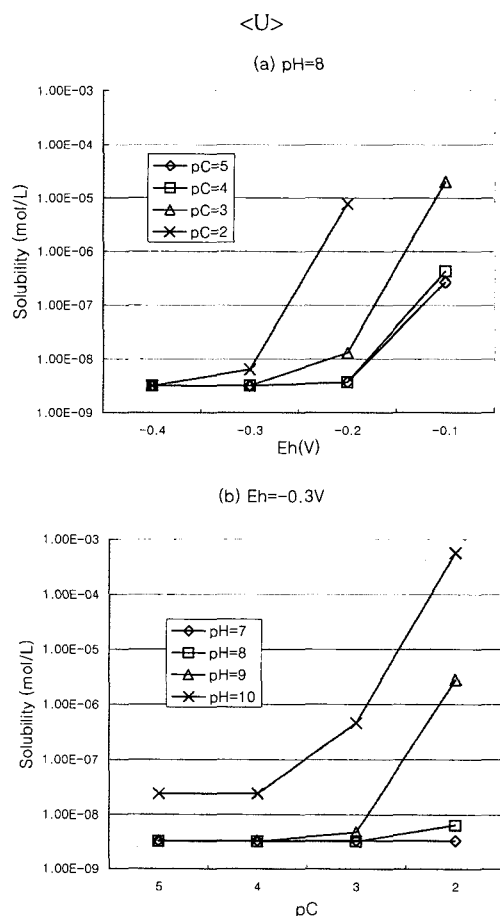


Fig. 3. Solubility of U as a Function of Eh, pH, and Total Carbonate Content

$E_h = -0.3V$, and $pC = 2$. The solubility becomes high at the condition where $UO_2(CO_3)_2^{2-}$, $UO_2(CO_3)_3^{4-}$, or both become predominant. However, it is not largely influenced by the variation of parameter values under strong reducing conditions where $U(OH)_4(am)$ controls the solubility, and the dominant aqueous species $U(OH)_4(aq)$ remains unchanged due to the stabilization of the species.

3.4. Neptunium

$Np(OH)_4(am)$ is the most predominant solubility-limiting-solid phase of neptunium under reducing conditions [7,15]. The calculated solubility agrees well within one order of magnitude with the

aqueous neptunium concentrations measured from spent fuel leaching tests [8~14].

Figure 4 shows the results of the sensitivity analysis with respect to the solubility of neptunium. The maximum and minimum solubility is $1.E-9$ and $1.E-7$ mol/L, respectively. The solubility is very sensitive to the carbonate concentration. The variation of solubility is entirely attributed to the difference in carbonate concentration. The dominant aqueous species changes from $Np(OH)_4(aq)$ to $Np(OH)_3CO_3^-$ with increasing carbonate concentration. Meanwhile, the solubility that is independent of E_h indicates that neptunium exists as only tetravalent states in solution. Furthermore, pH does not have a meaningful influence on the solubility because the dominant aqueous species remain unchanged. Therefore, we can conclude that neptunium would be a non-redox and non-pH sensitive element under natural granite groundwater conditions.

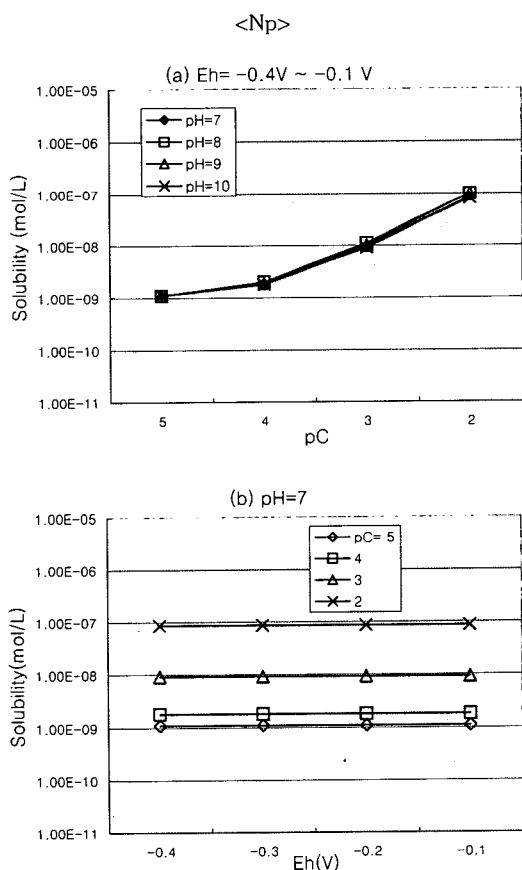


Fig. 4. Solubility of Np as a Function of E_h , pH, and Total Carbonate Content

3.5. Plutonium

The solubility of Pu in granite groundwater is known to be limited by the precipitation of $Pu(OH)_4(am)$ [7,15]. The calculated solubility is in good agreement with values obtained from spent fuel dissolution tests [8~14]. However, much lower concentration of plutonium is observed in natural waters, which can probably be ascribed to an additional sink term such as the sorption of plutonium onto particles.

The solubility of plutonium is between $4.0E-11$ and $2.8E-6$ mol/L within the range of parameter values studied (Table 2 or Figure 5). The highest solubility is obtained at the conditions of $pH = 7$ and $E_h = -0.4V$, where $Pu(III)$ aqueous species are predominant. The solubility is independent of the redox potential when tetravalent species are predominant (e.g., $E_h = -0.5 \sim -0.1V$, $pH = 9 \sim 10$, or $E_h = -0.2 \sim -0.1V$, $pH = 8$). With increasing

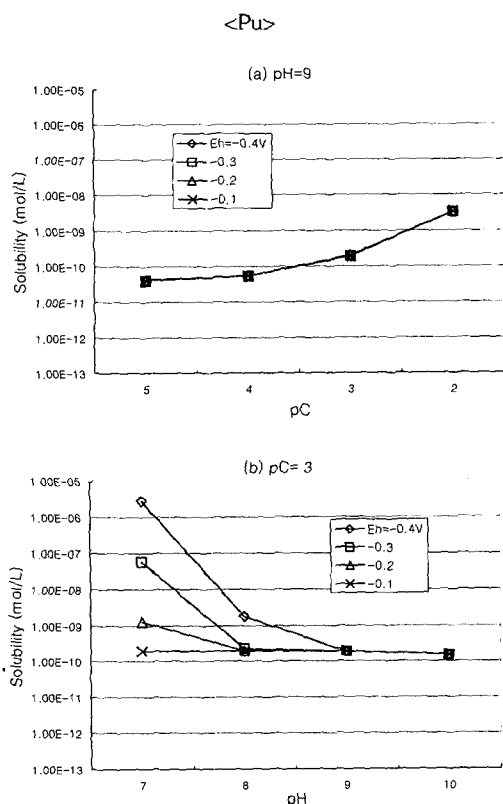


Fig. 5. Solubility of Pu as a Function of Eh, pH, and Total Carbonate Content

carbonate concentration, the dominant aqueous species of Pu(IV) changes from $\text{Pu}(\text{OH})_4(\text{aq})$ to $\text{Pu}(\text{OH})_3\text{CO}_3^-$, and the solubility becomes higher.

4. Conclusions

Redox potential, pH, and carbonate concentration of groundwater are known to be the most sensitive parameters controlling the solubility of actinides. These parameters vary along the pathway of groundwater and have an intrinsic uncertainty of measurement error. To be used as a source term for a performance assessment of HLW disposal, the uncertainty of solubility of actinides associated with the parameters should be investigated.

There is strong dependence of solubility and speciation of actinides with the variability of the above parameters. Within the range of parameter values found typically in natural granitic groundwater (pH=7 to 10, Eh=-0.4 to -0.1V, and carbonate concentration=1.E-5 to 1.E-2 mol/L), the calculated solubilities exist between 1.4E-10 and 1.6E-6 mol/L for Am, 4.9E-9 and 2.8E-6 mol/L for Th, 3.2E-9 and 5.7E-4 mol/L for U, 1.1E-9 and 1.0E-7 mol/L for Np, and 4.0E-11 and 2.8E-6 mol/L for Pu, respectively. Although the solubility of each actinide for the present groundwater condition is similar to that of the same element presented by other studies, the highest value obtained by an uncertainty analysis may be chosen as the solubility for the source term based on conservatism.

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