

Variation of Solubility for Uranium and Thorium Oxides with the Redox Potential Values of a KURT Ground Water

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1. Introduction

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 a spent nuclear fuel and related nuclear wastes in subsurface geological repositories. 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 a magnitude. The extent of a dissolution will also be controlled by the ligands present in a groundwater. 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). A comprehensive investigation of the predominant complexes of tetravalent actinides in a ternary system An(IV)-OH- CO_3 requires a variation of the concentrations of the ligands OH^- and CO_3^{2-} over wide ranges. In this study, the solubilities of UO_2 and ThO_2 in a domestic granitic ground water were measured experimentally in various conditions and their solubilities and speciations in the same conditions as the experimental solutions were also calculated by PHREEQC (V.2). Then these results were compared with each other as well as with foreign results.

2. Experiment and Calculation

The experiment was performed with 0.1 g of pretreated UO_2 and ThO_2 powders immersed in 400 mL of the KURT(KAERI Underground Research Tunnel) groundwater in a Teflon reaction vessel 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. Working and count electrodes were made of platinum plates with 5 cm^2 , and the count electrode was immersed into the groundwater isolated by a VycorTM membrane glass tube. 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. Sample solution was filtered to 0.22 μm and immediately re-filtered with an NMWL 500k membrane ultrafilter (3~5 nm pore size) to remove the colloids. Then the concentrations of uranium and thorium in the solutions were analyzed by an inductively coupled plasma - mass spectrometry.

$\text{UO}_2(\text{s})$ and $\text{ThO}_2(\text{s})$, which is suggested in "Chemical Thermodynamic Data Base 01/01" produced by Nagra/PSI¹, was used as the SLSP(solubility limiting solid phase) of uranium and thorium without a distinction between the crystal and amorphous compounds at $\text{pH} > 6$ of solution. 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).

3. Results

The variations of the concentrations of uranium and thorium in the sample solutions as a function of

dissolution the time are shown in Fig. 1. The solubility and species of the uranium and thorium in the same experimental solution conditions were calculated by PHREEQC and the results are shown Table 1.

4. Conclusions

The concentrations of uranium and thorium released from $UO_2(cr)$ and $ThO_2(cr)$ remained between $6 \times 10^{-8} \sim 10^{-9}$ mole/L in the KURT groundwater at a range of pH 8.1 ~ 11.4 and below -0.2 V of a reducing condition, which are comparable to foreign experimental results. The concentrations of uranium and thorium calculated by PHREEQC for $UO_2(s)$ and $ThO_2(s)$ in the same experimental solution conditions were $1.9 \times 10^{-7} \sim 7.8 \times 10^{-10}$ mole/L. This range is not greatly different from the experimental results.

REFERENCES

[1] W. Hummel U. Berner E. Curti F. J. Pearson T. Thoenen, Nagra/PSI Chemical Thermodynamic data base 01/01, Universal Publishers, Florida, USA, (2002).

Table 1. 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)
$UO_2(s)$	8.1	-0.2	7.8×10^{-10}
	9.8	-0.3	4.0×10^{-9}
	11.4	-0.4	7.1×10^{-9}
$ThO_2(s)$	8.1	-0.2	1.9×10^{-7}
	9.8	-0.3	1.0×10^{-7}
	11.4	-0.4	3.3×10^{-8}

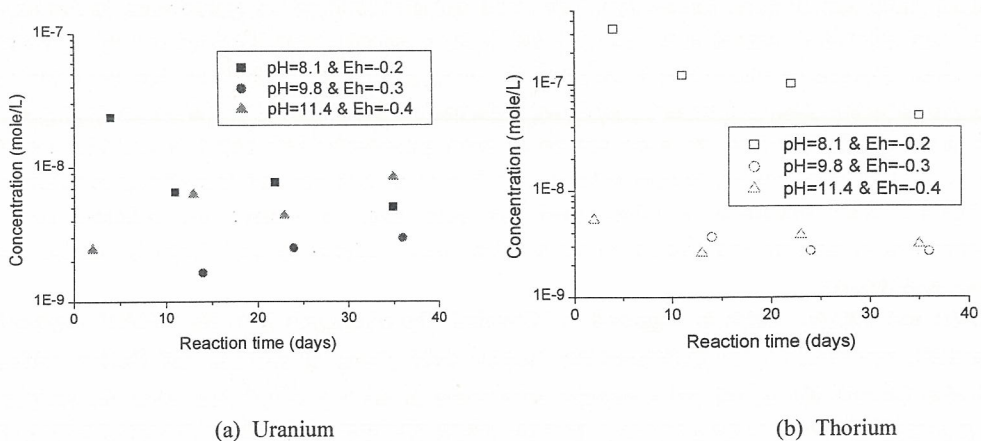


Fig. 1. The variation of the concentration of (a) uranium and (b) thorium at various pH and redox potential (Eh) as a function of a dissolution time.