

Geochemical Modeling of U Solubility in Groundwater Conditions

Young Hwan Cho, Kyung Won Han and In Suk Suh

Korea Advanced Energy Research Institute

(Received June 13, 1989)

지하수에서의 우라늄 용해도에 대한 지화학적 모델링 연구

조영환 · 한경원 · 서인석

한국에너지연구소

(1989. 6. 13 접수)

Abstract

Uranium solubilities have been calculated for a range of conditions expected in a nuclear waste disposal repository. Variables taken into consideration include the pH and Eh range expected for deep groundwaters, the effect of the composition of groundwater. The model used in these calculations is based on the assumption of chemical equilibrium. Calculations show that the major variables influencing uranium solubility under the repository conditions are pH and Eh. The results of this study can be applied to an assessment of the nuclear waste disposal.

요 약

처분장에서 예상되는 주요 지중변수들의 광범위한 조건에서 우라늄의 용해도를 계산하였다. 고려된 변수로는 pH, Eh 및 지하수의 조성을 선정하였다. 계산에는 열역학적 화학평형 법칙에 원리를 두고 있다. 결과, 지하 처분장의 예상조건에서 우라늄의 용해도에 영향을 미치는 중요한 변수는 Eh, pH 임을 보여준다. 본 연구결과는 방사성폐기물 처분 안전성 평가에 적용할 수 있다.

Introduction

The solubility of uranium in natural groundwater is of interest from two viewpoints. This has been studied in relation to the formation and dissolution of uranium ores.[1] But, recently this study has become of great importance in relation to the nuclear waste disposal. The solubility of uranium under repository conditions

is an important parameter in modeling the radionuclide release from the radioactive waste matrix that is starting process of radionuclide migration. The thermodynamic properties of dissolved uranium species can be used to compute solution equilibria relations and give equilibrium concentrations. These theoretical approaches help understand conditions of formation of uranium deposits, and may be applied to safety

assessment of nuclear waste disposal. One of the parameters important to disposal safety assessment is the degree to which radioactive waste dissolves in natural groundwater. In this study, the uranium solubilities have been modelled with respect to Eh, pH and groundwater composition.

Principle of Calculation

The model used in this calculation is based on the assumption of chemical equilibrium, using relationships which were derived from the laws of thermodynamics. The results reported here were computed using SOLMNQ.[2] Computer code SOLMNQ is an interactive chemical equilibrium code that calculates equilibrium distribution of aqueous inorganic species in natural groundwater. This is a modified version of SOLMNEQ, tha was originally developed in U.S. Geological Survey, with extended database including updated uranium and plutonium data. By using this SOLMNQ, the uranium solubility can be calculated in

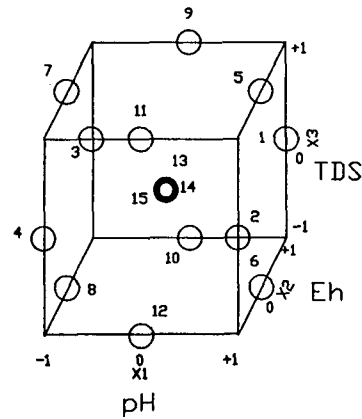


Fig. 1-b. Design Diagram of 3-level, 3-variable Box-Behnken model

a given pH, Eh and groundwater composition.

A three-level, three variable statistically designed format[3] (Box-Behnken Model) was used to quantify the effects of variables on the uranium solubility. This format was shown in the Fig. 1-a, b. These figures represents the design matrix and diagram of the model used in this study. Table 1 represents the coded and actual values of the variables used in this study.

According to this model, total 15 data points are needed. Those are twelve center-edge and 3 center point in triplicate of the design cube. Uranium solubility data on above data points of the the design cube are used to produce an mathematical equation relating the

#	Run #	X ₁	X ₂	X ₃	X ₁ ²	X ₂ ²	X ₃ ²	X ₁ X ₂	X ₁ X ₃	X ₂ X ₃
1	13	0	0	0	0	0	0	0	0	0
2	10	0	1	-1	0	1	1	0	0	-1
3	3	-1	1	0	1	1	0	-1	0	0
4	9	0	1	1	0	1	1	0	0	1
5	1	1	1	0	1	1	0	1	0	0
6	12	0	-1	-1	0	1	1	0	0	1
7	8	-1	0	-1	1	0	1	0	1	0
8	6	1	0	-1	1	0	1	0	-1	0
9	4	-1	-1	0	1	1	0	1	0	0
10	11	0	-1	1	0	1	1	0	0	-1
11	7	-1	0	1	1	0	1	0	-1	0
12	15	0	0	0	0	0	0	0	0	0
13	2	1	-1	0	1	1	0	-1	0	0
14	5	1	0	1	1	0	1	0	1	0
15	14	0	0	0	0	0	0	0	0	0

Fig. 1-a. Design matrix of 3-level, 3-variable Box-Behnken model

Table 1. Level and values of the variables used in this study

Variables	Coded Levels		
	-1	0	+1
X ₁ (pH)	5.0	7.0	9.0
X ₂ (Eh)	-0.5	+0.25	+1.0
X ₃ [log (TDS)]	4.056	3.056	2.056

X₁ (pH) : hydrogen ion concentration

X₂ (Eh) : electrochemical potential of groundwater (in Volt)

X₃ (TDS): total dissolved solids (mg/L)

effects of 3 geochemical variables on uranium solubility.

Table 2 lists the reactions and their equilibrium constants used in uranium solubility calculation. caclualtion (4).

Table 2. Uranium Reaction and Their Equilibrium Constants (T=25°C) used for Calculation

log [K eq]	Reactions
-12.00	$U^{3+} \rightleftharpoons U^{4+} + e^{-}$
0.65	$U(OH)^{3+} + H^{+} \rightleftharpoons U^{4+} + H_2O$
2.47	$U(OH)_2^{2+} + 2 H^{+} \rightleftharpoons U^{4+} + 2 H_2O$
5.43	$U(OH)_3^{+} \rightleftharpoons U^{4+} + 3 OH^{-}$
9.59	$U(OH)_4 \rightleftharpoons U^{4+} + 4 H_2O$
15.10	$U(OH)_5^{-} + 5 H^{+} \rightleftharpoons U^{4+} + 5 H_2O$
-8.77	$UO_2 + 4 H^{+} + e^{-} \rightleftharpoons U^{4+} + 2 H_2O$
-12.57	$UO_2^{2+} + 4 H^{+} + 2 e^{-} \rightleftharpoons U_4 + 2 H_2O$
5.78	$UO_2(OH)^{+} + H^{+} \rightleftharpoons UO_2^{2+} + H_2O$
5.62	$(UO_2)_2(OH)_2^{2+} \rightleftharpoons 2 UO_2^{2+} + 2 H_2O$
15.64	$(UO_2)_3(OH)_3^{+} + 5 H^{+} \rightleftharpoons 3 UO_2^{2+} + 5 H_2O$
30.75	$(UO_2)_3(OH)_3 \rightleftharpoons 3 UO_2^{2+} + 7 H_2O$
11.93	$UO_2(OH)_2 + 2 H^{+} \rightleftharpoons UO_2^{2+} + 2 H_2O$
-10.06	$UO_2CO_3 \rightleftharpoons UO_2^{2+} + CO_3^{2-}$
-17.08	$UO_2(CO_3)_2^{2-} \rightleftharpoons UO_2^{2+} + 2 CO_3^{2-}$
-21.48	$UO_2(CO_3)_3^{4-} \rightleftharpoons UO_2^{2+} + 3 CO_3^{2-}$
-2.59	$UCl^{3+} \rightleftharpoons U^{4+} + Cl^{-}$
-8.65	$UF^{3+} \rightleftharpoons U^{4+} + F^{-}$
-14.47	$UF_2^{+} \rightleftharpoons U^{4+} + 2 F^{-}$
-19.07	$UF_3 \rightleftharpoons U^{4+} + 3 F^{-}$
-23.67	$UF_4 \rightleftharpoons U^{4+} + 4 F^{-}$
-25.29	$UF_5^{-} \rightleftharpoons U^{4+} + 5 F^{-}$
-27.61	$UF_6^{2-} \rightleftharpoons U^{4+} + 6 F^{-}$
-5.18	$UO_2F^{+} \rightleftharpoons UO_2^{2+} + F^{-}$
-8.90	$UO_2F_2 \rightleftharpoons UO_2^{2+} + 2 F^{-}$
-11.40	$UO_2F_3^{-} \rightleftharpoons UO_2^{2+} + 3 F^{-}$
-12.49	$UO_2F_4^{2-} \rightleftharpoons UO_2^{2+} + 4 F^{-}$
-1.75	$UO_2Cl^{+} \rightleftharpoons UO_2^{2+} + Cl^{-}$
-8.41	$UO_2HPO_4 \rightleftharpoons UO_2^{2+} + HPO_4^{2-}$
-18.29	$UO_2(HPO_4)_2^{-} \rightleftharpoons UO_2^{2+} + 2 HPO_4^{2-}$
-10.23	$UO_2H_2PO_4 \rightleftharpoons UO_2^{2+} + HPO_4^{2-} + H^{+}$
-19.88	$UO_2(H_2PO_4)_2 \rightleftharpoons UO_2^{2+} + 2 HPO_4^{2-} + 2 H^{+}$
-28.79	$UO_2(H_2PO_4)_3^{-} \rightleftharpoons UO_2^{2+} + 3 HPO_4^{2-} + 3 H^{+}$

-12.05	$UHPO_4^{+} \rightleftharpoons U^{4+} + HPO_4^{2-}$
-21.99	$U(HPO_4)_2 \rightleftharpoons U^{4+} + 2 HPO_4^{2-}$
-30.69	$U(HPO_4)_3^{-} \rightleftharpoons U^{4+} + 3 HPO_4^{2-}$
-38.70	$U(HPHO_4)_4^{2-} \rightleftharpoons U^{4+} + 3 HPO_4^{2-}$
-5.54	$USO_4^{+} \rightleftharpoons U^{4+} + SO_4^{2-}$
-9.84	$U(SO_4)_2 \rightleftharpoons U^{4+} + SO_4^{2-}$
-2.95	$UO_2SO_4 \rightleftharpoons UO_2^{2+} + SO_4^{2-}$

Results and Discussion

In order to estimate uranium solubilities in the expected repository conditions, three important geochemical variables were taken into account.

The modelled standard groundwater[5] representing saline groundwater found at 500 m level of granitic pluton was used as reference for this calculation. The composition of reference groundwater was shown in Table 3. Ten and one percent dilutions of this was used as $X_3 = 0$ and -1 , respectively. And pH ranges of 5 to 9 were chosen for this study because it represents the upper and lower boundary of natural groundwater and Eh range was from -0.5 V to $+1$ V representing strong reducing to highly oxidizing conditions.

Total 15 uranium solubility data were obtained by

Table 3. Composition of standard groundwater used in this study

Components	mg/L	Molarity
Na	1910	8.40 E-2
K	14	3.62 E-4
Mg	61	2.54 E-3
Ca	2130	5.38 E-2
Sr	24	2.77 E-4
Fe	0.56	1.01 E-5
Fe	0.56	1.01 E-5
Si	5	1.80 E-4
HCO3	68	1.13 E-3
Cl	6086	1.74 E-1
SO4	1040	1.10 E-2
NO3	33	5.38 E-4
F	2	1.06 E-4

Table 4. Uranium solubility calculated by SOLMNQ and fitted model equation

No.	Run #	Variable & level			U solubility Mole/L	
		X ₁	X ₂	X ₃	by. SOLMNQ	Regression Equation
1	13	0	0	0	-5.64016	-5.64054
2	10	0	1	-1	-4.95860	-4.90293
3	3	-1	1	0	-2.79588	-2.97598
4	9	0	1	1	-3.90657	-3.71741
5	1	1	1	0	-4.43889	-4.50349
6	12	0	-1	-1	-12.9469	-13.1390
7	8	-1	0	-1	-6.00305	-5.87756
8	6	1	0	-1	-4.50307	-4.49233
9	4	-1	-1	0	-14.2097	-14.1450
10	11	0	-1	1	-12.8356	-12.8901
11	7	-1	0	1	-4.70114	-4.71226
12	15	0	0	0	-5.64016	-5.64054
13	2	1	-1	0	-10.9244	-10.7432
14	5	1	0	1	-4.09745	-4.22322
15	14	0	0	0	-5.64016	-5.64054

running SOLMNQ according to the design format. All the calculations were done at T=25°C.

As a result of multiple-regression using these data, the uranium solubility within the ranges of this study can be expressed as follows:

$$\begin{aligned} \log[\text{U solubility}] = & -5.640 + 0.4686 X_1 \\ & + 4.3522 X_2 + 0.3586 X_3 + 0.6923 X_1^2 \\ & - 3.143 X_2^2 + 0.1219 X_3^2 \\ & - 1.232 X_1 X_2 - 0.224 X_1 X_3 + 0.2342 X_2 X_3 \end{aligned}$$

$$\text{where, } X_1 = \frac{(\text{pH} - 7)}{2}$$

$$X_2 = \frac{(\text{Eh} - 0.25)}{0.75}$$

$$X_3 = \log[\text{TDS}] - 3.056$$

Table 4 lists the calculated uranium solubilities by using SOLMNQ, and fitted model regression equation. Table 5 lists the results of regression analysis.

The effects of each variables on uranium solubilities are shown in Fig. 2-a, b, c and Fig. 3-a, b, c which

Table 5. Results of regression calculation

Regression coefficients		Standard deviation	R square value
b ₀	-5.640	0.1917	0.9991
b ₁	0.4686	0.0678	
b ₂	4.3522	0.0678	
b ₃	0.3586	0.0678	
b ₁₁	0.6923	0.0997	
b ₂₂	-3.143	0.0997	
b ₃₃	0.1219	0.0997	
b ₁₂	-1.232	0.0958	
b ₁₃	-0.224	0.0958	
b ₂₃	0.2342	0.0958	

were drawn by using regression equation. These results shown that expected uranium solubilities in the repository conditions are very low, that is of the order of 10⁻¹⁰ M or 0.02 ppb. This value is in agreement with uranium concentrations found in naturally occurring groundwaters in reducing environments[6] and

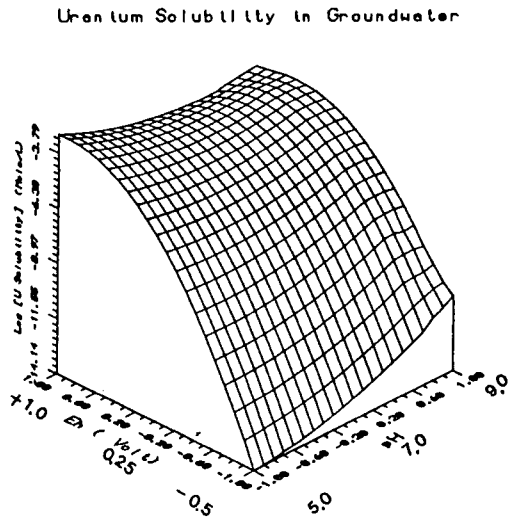


Fig. 2a. Effects of Eh and pH on U Solubility

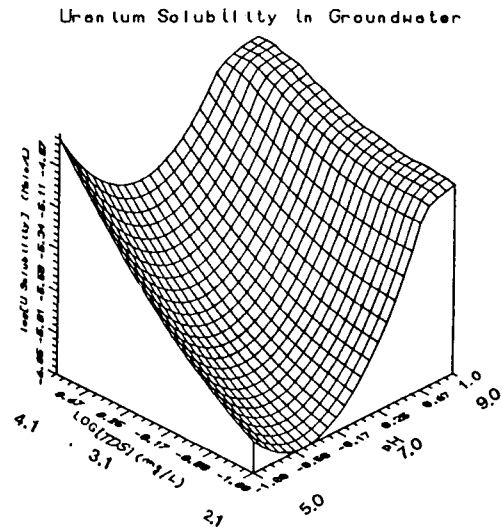


Fig. 2b. Effects of TDS and pH on U Solubility

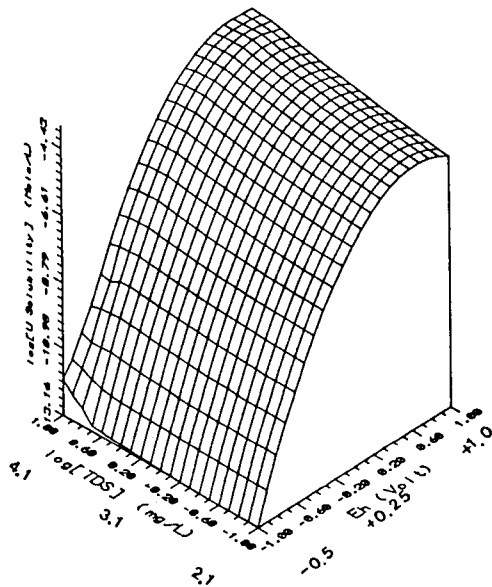


Fig. 2c. Effects of Eh and TDS on U Solubility

laboratory experimental results under similar conditions.[7]

Fig. 2-a shows the effect of redox potential and pH on the uranium solubility at a fixed TDS, 3.1 mg/L. Solubility is strongly dependent on redox potential. In an oxidizing conditions, solubility is several orders of magnitude greater than that of in a reducing condi-

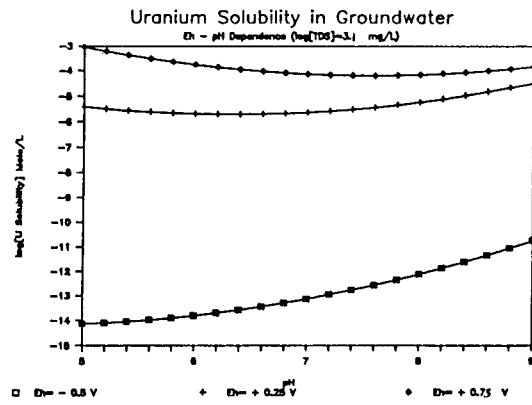


Fig. 3a. Effects of Eh and pH on U Solubility

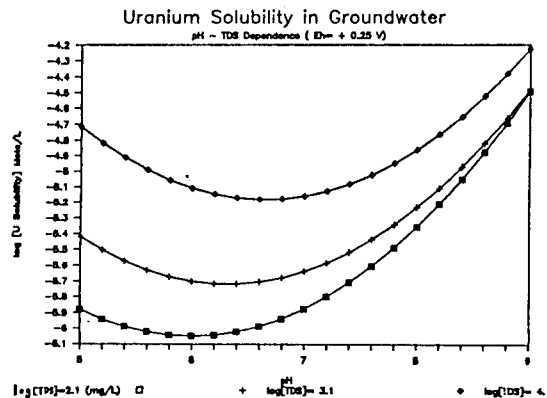


Fig. 3b. Effects of TDS and pH on U Solubility

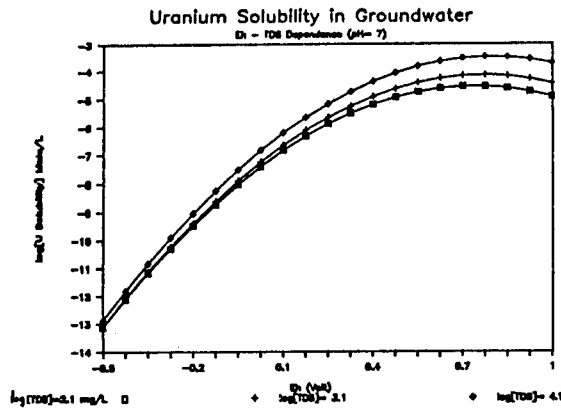


Fig. 3c. Effects of Eh and TDS on U Solubility

tions. The effect of pH is not so much crucial than redox potential.

Fig. 2-b shows that effect of pH and total dissolved solids on uranium solubility at fixed redox potential of 0.25 Volt.

Uranium solubility is highly dependent on pH conditions. This shows that a slightly acidic condition is the optimum condition for lowering uranium solubility. The solubility increases with increasing total dissolved solid contents. This is because of complex formation with anionic ligands in the groundwater. As the concentration of anionic ligand increases, the amounts of aqueous uranium complexes increases. This complex formation contributes to the uranium solubility. In a given slightly oxidizing redox condition (+0.25 V), uranium solubility is minimum at a little acidic conditions.

Fig. 2-c show the effect of redox potential and TDS on the uranium solubility at a neutral pH condition. As expected, the U solubility is strongly dependent on redox-potential.

The modeling results of this study, strongly supports the in-situ mining and processing of uranium. The solubility of uranium increases in oxidizing and highly acidic or alkaline conditions. Also strong complexing ligands like carbonates increases the solubility. In fact, ammonium carbonate is used in leaching of uranium from the ore.

In order to increase uranium solubility in the process, acid leaching as well as base leaching method is used along with appropriate oxidizing agents.

Although there may exist limitations due to the complex nature of reactions and uncertainties in the thermodynamic database it is expected that they will not influence the results by more than one or two orders of magnitude.

Applications and Conclusion

Nature itself shows the evidence of stability of uranium in the underground conditions. Observations made on the natural reactor discovered at Oklo[8] suggests that irradiated uranite grains have remained intact for over a billion years. The stability of uranium oxide in groundwater has been confirmed by studies at the Cigar Lake uranium deposit in northern Canada as a natural analog for nuclear waste disposal.[9] Water samples taken only 5 m from the ore body have a uranium concentration less than $1 \mu\text{g/L}$ and are well below levels for drinking waters. The calculated results of this study supports this. The results of this study suggests that the environment of the ideal nuclear waste disposal repository condition would include a groundwater which is buffered at a slightly acidic to near neutral pH and at a moderately reducing Eh. This environment may be reinforced by the addition of suitable materials to the low permeability backfill surrounding the wastes.

The knowledge of the parameters affecting uranium solubility can be used as a feedback data in the design of engineered barriers and in the evaluation of a suitable repository site.

Acknowledgement

The authors are indebted to Dr. B. Goodwin and T.T Vandergraaf for providing SOLMNQ and helpful guidance during author's attachment at Atomic Energy of Canada Limited (AECL).

References

1. R.M. Garrels and C.L. Christ, "solutions, Minerals and Equilibria, harper and Row, New York, (1965)
2. B.W. Goodwin and M. Munday, "A Reference Guide to SOLMNQ—An Interactive Solution-Mineral Equilibrium Program.", AECL-7800, AtomicEnergy of Canada Limited, (1983)
3. G.E.P. Box and D.W. Behnken, "Some New Three-Level Designs for the Study of Quantitative Variables.", *Technometrics* 2, 673-680 (1960)
4. R.J. Lemire and P.R. Tremaine., "Uranium and Plutonium Equilibria in Aqueous Solutions to 200°C.", *J. Chem. Eng. Data*, 25, 361 (1980)
5. M.Gascoyne, "Reference Groundwater Composition for a Depth of 500 m in the Whiteshell Research Area.", TR-243, Atomic Energy of Canada Limited (1988)
6. J.K. Osmond and J.B. Cowart, "The Theory and Use of Natural Uranium Isotopic Variations in Hydrology.", *Atomic Energy Review* 14, 621-674 (1976)
7. P.R. Tremaine, et al. "Solubility of uranium (IV) oxide in alkaline aqueous solutions to 300°C.", *J. Solution Chem.*, 10, 221 (1981)
8. G.A. Cowan., "Migration paths for Oklo reactor products and application to the problem of geological storage of nuclear waste.", IAEA-TC-119. p.693, (1978)
9. J.J. Cramer, "A Natural Analog for a Nuclear Fuel Waste Disposal Vault.", *Proceedings of the 2nd International Conference on Radioactive Waste Management*, Winnipeg, Canadian Nuclear Society, 1986 September.