Solubility of Neptunium in the KAERI Underground Research Tunnel (KURT) using PHREEQC

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1. Introduction

For the safety of the permanent HLW disposal, chemical properties of radionuclides under the geological environmental condition are important when water intrudes into repository and a leakage occurs. Neptunium is one of the primary actinides of fundamental concern for the long-term storage of nuclear waste due to the long half-lives (^{237}Np : $T_{1/2}$ = 2.14×10^6 yrs), and different transport characteristics under varying conditions [1]. Neptunium is redox sensitive element and has mainly two oxidation states (Np^{4+}, NpO_2^+) stable in aqueous condition. Different oxidation states and chemical species provide different chemical properties, such as solubility, sorption etc. Under reducing condition, the dominant oxidation state is Np(IV). Therefore, the repository is constructed under deep geologic condition. However, after a leakage occurs, the redox condition in the near-field is changed by radiolysis of water and by interaction with canister and backfill materials. Therefore understanding of chemical properties depending on E_h, pH under different groundwater conditions is inevitable. For the evaluation of behavior of neptunium, the present work aims for the analysis of solubility and distribution of chemical species under different groundwater conditions.

2. Geochemical Modeling

Calculation of solubility and analysis of chemical species were performed with geochemical modeling program PHREEQC 2.0 based on the updated OECD-NEA thermodynamic database [2]. Neptunium species without experimental evidences of the formation are not included in this work.

Groundwater samples were originated from the borehole YS-01 in KAERI Underground Research Tunnel (KURT) at three different depths [3]. Table I shows the major compositions in each groundwater. A significant difference is E_h value. YS-1-3 groundwater sample has oxidizing condition, whereas YS-1-4 and YS-1-6 groundwater samples have reducing conditions.

Table I: Composition and characteristics of the groundwater samples from the borehole YS-01 in KURT

Sample No.	Depth (m)	Temp. (°C)	pH	E_h	Alk. (x1000)
YS-1-3	169.5	17.6	10.71	63	0.73
YS-1-4	259.5	19.8	10.23	-109	0.96
YS-1-6	457.5	24.5	9.93	-142	0.75
Sample No.	Na^+	K^+	Ca^{2+} (mg/L)	SiO_2	HCO_3^-
YS-1-3	25.0	1.14	5.7	27.4	3.9
YS-1-4	35.8	0.60	6.2	25	6.4
YS-1-6	36.9	0.58	2.4	18.2	1.7
Sample No.	CO_3^{2-}	F^-	NO_3^- (mg/L)	SO_4^{2-}	Cl^-
YS-1-3	7.7	8.1	3.7	2.0	3.0
YS-1-4	0.0	13.9	17.1	11.5	2.2
YS-1-6	0.2	9.0	20.1	12.1	3.8

3. Results and Discussion

3.1 Solubility and Distribution of Chemical Species

The solubility of neptunium in each groundwater is calculated using PHREEQC 2.0. The solubility of neptunium is controlled by the precipitation of the tetravalent hydrous oxides $NpO_2 \cdot nH_2O$ [4]. Fig. 1 represents a solubility curve as a function of pH. NpF_2^{2+} and $NpO_2(OH)_2^-$ affect increasing of solubility at low and high pH, respectively. At pH > 9, formation of $NpO_2CO_3^-$ contributes to higher solubility in YS-1-3 groundwater.
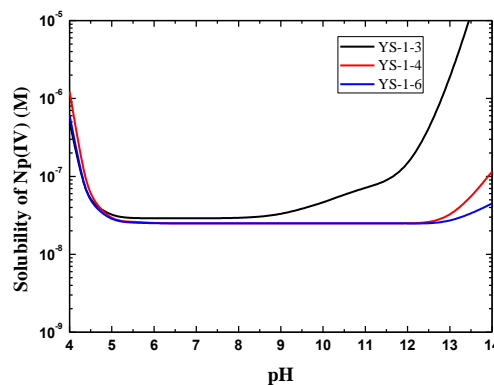

Fig. 1. Solubility of Np(IV) as a function of pH

Table II shows the solubility in each groundwater samples. Due to the formation of neptunium carbonate

complex as a dominant species, solubility becomes higher under oxidizing condition (YS-1-3).

Table II: Solubility of neptunium

	Solubility (mol/L)	Species
YS-1-3	6.7×10^{-8}	$NpO_2CO_3^-$: 54.25 %
		$Np(OH)_4(aq)$: 37.85 %
YS-1-4	2.5×10^{-8}	$Np(OH)_4(aq)$: 99.92 %
YS-1-6	2.5×10^{-8}	$Np(OH)_4(aq)$: 100 %

Experimentally determined solubility in KURT groundwater are found in the concentration range of between $6.0 \times 10^{-8} \sim 2.0 \times 10^{-8}$ mol/L at pH 9.5 ~ 11.1 under E_h = -0.2 V. The results are in excellent agreement with the calculated solubility data.

The Pourbaix (E_h - pH) diagrams are calculated under the condition of YS-01 groundwater samples (Fig.2).
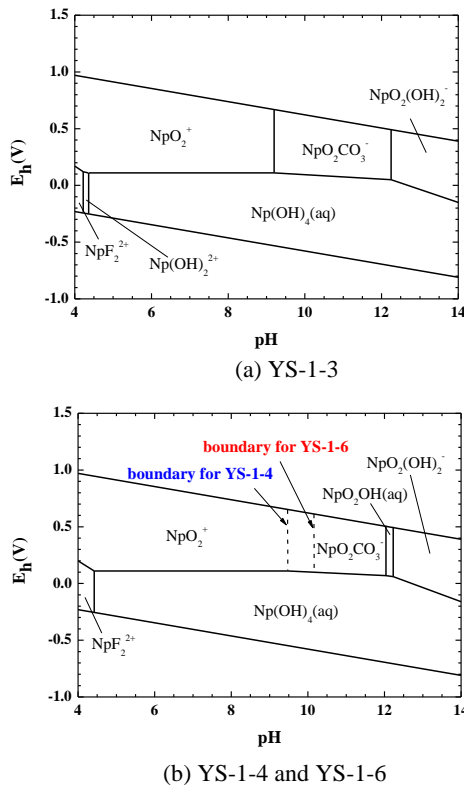

(a) YS-1-3

(b) YS-1-4 and YS-1-6
Fig. 2. Pourbaix diagram for Np in groundwaters

The distribution of chemical species of Np is not affected significantly by groundwater compositions. In the neutral to alkaline solution (pH 5 ~ 11, E_h -0.2 ~ +0.6 V), the distribution of chemical species is identical among three groundwater. Under reducing condition (E_h < 0), NpF_2^{2+} and $Np(OH)_4(aq)$ are dominant species at lower pH and higher pH, respectively. At high pH and E_h > 0, neptunium carbonate complex, $NpO_2CO_3^-$, is predominant. The carbonate complexes contribute to increase of solubility, as shown in Fig. 3.

3.2 Carbonate effect

In the YS-01 groundwater, the amount of carbonate concentration is not significant. In the present work, simulation of carbonate effect is performed in case that carbonate concentration increases under repository conditions. As shown in Fig. 3, carbonate effect become pronounced when total carbonate concentration is greater than 1.0×10^{-2} mol/L. Formation of $Np(CO_3)_4^{4-}$ and $Np(CO_3)_5^{6-}$ affect the increase of solubility. When the total carbonate concentration is lower than 1.0×10^{-2} mol/L, $Np(OH)_4(aq)$ is the dominant species.
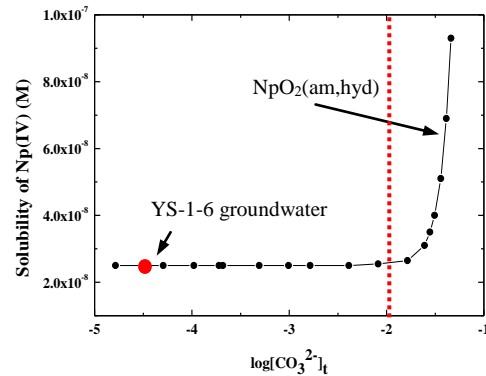

Fig. 3. Solubility of Np(IV) as a function of carbonate concentration in YS-1-6 groundwater

4. Conclusions

In this study, the solubility and distribution chemical species of neptunium in KURT groundwater are investigated using PHREEQC 2.0. The calculated solubility remained between $6.7 \times 10^{-8} \sim 2.5 \times 10^{-8}$ mol/L. This result corresponds with experimental results. The distribution of neptunium chemical species is not changed significantly under various groundwater conditions. The dominant species is $Np(OH)_4(aq)$ and $NpO_2CO_3^-$ under reducing and oxidizing condition, respectively. The carbonate effect on solubility is notable when the total carbonate concentration is greater than 1.0×10^{-2} mol/L.

REFERENCES

[1] Dozol, M., Hagemann, R., Hoffman et al., *"Radionuclide migration in groundwaters: review of the behaviour of actinides"*, Pure Appl. Chem. **65**, 1081–1102.(1993)
[2] R. Guillaumont et al., *"Update on the Chemical Thermodynamics of Uranium, Neptunium, Plutonium, Americium and Technetium"*, Volume **5**, Edited by OECD Nuclear Energy Agency and Data Bank Issy-Les-Moulineaux, ELSEVIER, 2003.
[3] D. S. Bae, C.S. Kim, K.S. Kim et al., *"High-Level Radwaste Disposal Technology Development-Assessment of Deep Geological Environmental Condition,"* KAERI /RR-2783/2006, Korea Atomic Energy Research Institute, Daejeon, 2007.
[4] T. E. Eriksen, P. Ndalamba et al., "*Solubility of the redox-sensitive radionuclides ^{99}Tc and ^{237}Np under reducing conditions in neutral to alkaline solutions. Effect of carbonate"*, SKB Technical report 93-18 (1993).