Variation of Solubility for Nepunium Oxide with the Redox Potential in a Domestic Ground Water

Seung Soo Kim, Min Hoon Baik, Kwang Cheol Kang, Han Beom Yang and Jong Won Choi

Korea Atomic Energy *Research Institute, 1045, Daedeok-daero, Yuseong-gu, Daejeon, 305-353, Korea*

nsskim@kaeri.re.kr

1. Introduction

The spent UO_2 fuel contains 0.02 ~ 0.1% neptunium as NpO_2. Neptunium is one of the primary concern radioelements for the disposal of nuclear waste at the proposed repository. This is due to its long half-life, radiotoxicity, and transport property especially under oxidizing conditions where NpO_2^+ and/or $NpO_2CO_3^-$ are predominant. However $Np(OH)_4(aq)$, known the dominant aqueous complex in neutral solution under reducing conditions, are less soluble, and the high tendency of Np(IV) ions to form aqueous complexes produces strong interactions with the geomatrix.

Generally the experimental measurement of a speciation of an actinide in a reducing groundwater with pH>7 is very difficult because 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 of relatively simple compositions, several geochemical codes have been developed in order to estimate the solubility of nuclides.

In this study, the solubilities of $NpO_2(s)$ in a domestic granitic groundwater were measured experimentally in various conditions and its solubility and speciation in the conditions were calculated by a geochemical code. Then these results were compared with each other as well as with literature results.

2. Experiment and Calculation

The experiment was performed with 30 mg of NpO_2 powder put into about 400 mL of the KURT groundwater in a Teflon reaction vessel in an Ar-filled glove box at room temperature. The redox potential (Eh) of the groundwater was adjusted to around -0.2, -0.3 and -0.44 V by a potentiometer. The sample solutions from a reaction vessel were drawn periodically and filtered with an NMWL 500k membrane ultrafilter to remove the colloids. Then their radioactivity of Np-237 were measured by an liquid scintillation analyzer.

For the calculation of the solubility and dissolved species of neptunium, thermodynamic data of OECD/NEA, Nagra/PSI, KAERI and JNC were compared in this study. The formation constants of $Np(OH)_4(aq)$ and the solubility products of $NpO_2(am, hyd)$ are different between OECD-NEA and Nagra/PSI. So both institutes' data were separately used the calculation of the solubility of neptunium in the KURT groundwater. Though the existence evidence of the ternary complexes of Np(IV) ($Np(OH)_x(CO_3)_y^{4-x-2y}$) and their equilibrium constants have been a controversial, the complexes were also considered to explain our experimental results.

3. Results and Discussion

Experimental results for the neptunium concentrations in the KURT groundwater with a different pH and Eh are illustrated in Fig. 1 with the literature results. In this figure, the neptunium concentrations at pH = 9.5, 10.2 and 11.1 were obtained in the solution with around -0.2V of Eh, and the concentrations at pH = 11.8 and 13 were obtained Eh = -0.3 and -0.4V solution, respectively. As shown Fig. 1, the concentration of neptunium released from NpO_2 into the KURT groundwater remained between $6x10^{-8}$ ~ $2x10^{-8}$ mole/L at the range of pH 9.5 ~ 11.1 under around -0.2 V while the concentration decreased to less than $5x10^{-9}$ mole/L at

pH=11.8 ~ 13 and below -0.3 V. Our results at around Eh = -0.2V are a little higher than the our and literature values calculated with geochemical codes. However generally foreign experimental concentrations also are a little higher than calculation values, and they are similar to our results.

The increase solubility of neptunium at pH = 8 ~ 11, compared to a carbonate-free solution, may be explained by the formation of the ternary complexes. In a Eriksen's experiment, the Np(IV) concentration dissolved from $Np(OH)_4(s)$ in 1 mM bicarbonate solution at pH = 9.2 was about 6×10^{-8} mole/L. The solubility and dominant species of neptunium in a fresh-reducing-high pH bentonite porewater for $NpO_2(am)$ in JNC-Tokai Works were calculated as 2×10^{-8} mole/L and $Np(OH)_2(CO_3)_2^{2-}$ and $Np(OH)_4(aq)$. In order to clearly understand the neptunium solubility, the identification of the $Np(OH)_x(CO_3)_y^{4-x-2y}$ complexes and their thermodynamic data, and the certification of the reaction constants of $Np(OH)_4(aq)$ and $NpO_2(am, hyd)$, etc. have to be studied in the future.

4. Conclusions

The concentration of neptunium released from $NpO_2(s)$ into the KURT groundwater remained between 6×10^{-8} ~ 2×10^{-8} mole/L at the pH range of 9.5 ~ 11.1 under around -0.2 V of a reducing condition while the concentration decreased to less than 5×10^{-9} mole/L at a pH=11.8 ~ 13 and below -0.3 V. The higher concentrations of neptunium ($> 1 \times 10^{-8}$ mole/L) at a reducing condition may be due to the ternary complexes $Np(OH)_x(CO_3)_y^{4-x-2y}$ though their existence and their equilibrium constants were not clearly certified.
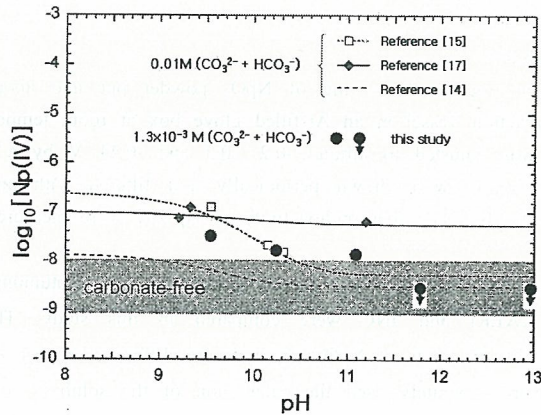

Fig. 1. The comparison of our and literature results for the solubility of neptunium at various pH and carbonate concentration. 🔻 indicates below detection limit (5×10^{-9} mole/L) of LSC.

15. A. Kitamura, Report JNC TC8400 2001-006, 2001.

17. T. E.Eriksen, SKB-TR-93-18, 1993.

14. D. Rai, Radiochim. Acta Vol.84 159, 1999.