

Solubility Behavior of Pu(IV) in EDTA and ISA Containing Aqueous Solution

S.Y. Park^{a*}, B.S. Choi^a, W.K. Choi^a, and W. D. Schecher^b

^aDecontamination and Decommissioning Research Div., KAERI, 989-111 Daedeok-daero, Yuseong, Daejeon 34057, Rep. of Korea

^bEnvironmental Research Software 16 Middle Street, Hallowell, ME 04347

*Corresponding author: nsypark@kaeri.re.kr

1. Introduction

The KORAD waste disposal site built in Gyeongju opened in 2014 and has been operating until now. When the disposal of radioactive waste is completed and the repository is closed, it must be stored for a long period of more than 5,000 years. During this period, oxygen is blocked from the outside and the reducing atmosphere is maintained for a long time due to the oxygen-free corrosion of the iron and steel material. Since most of the waste solidifying material and structural material of the repository use Portland cement, the pH of the groundwater introduced into the cement pores is maintained in a reducing atmosphere under high alkalinity conditions in the range of 10 - 13.3. When a radionuclide is exposed in such an atmosphere, solubility may be increased. Moreover, complexing agents such as EDTA, NTA, oxalic acid, and citric acid contained in the waste drum forms a complex with radionuclides increase the solubility and mobility of them[1].

Waste drums generated from domestic nuclear power plant generally contain about 30% cellulose[1]. When this waste drum containing cellulose is exposed to a strong alkaline atmosphere in a reducing atmosphere at a disposal site, it decomposes to generate complexing agents such as ISA[2]. These materials can also form a complex with radionuclides to increase solubility and nuclide mobility. Since such a phenomenon has a large impact on the safety and environment of the repository, the effect of complexing agents on the nuclide solubility should be evaluated. Plutonium has high alpha radiotoxicity and is a very long half-life nuclide ($t_{1/2, \text{Pu-239}} = 2.41 \times 10^4 \text{y}$). Under reducing conditions, the Pu(III) and Pu(IV) states are expected to dominate [3]. Therefore, it is very important to evaluate the effect of complexes on the solubility of Pu(III) and Pu(IV) in a repository environment containing complexes.

In this study, the speciation and solubility behavior of Pu(IV) ions in aqueous solutions containing EDTA and ISA were investigated. After collecting thermodynamic data from literature, optimal data were selected and ionic strength were compensated to fit for MINEQL program. The speciation of each ionic species and complex species was calculated through the MINEQL program. The critical ISA concentration affecting the solubility of Pu(IV) was determined and the effect of Pu(IV)-ISA or Pu(IV)-EDTA complex species on the solubility was investigated.

2. Methods and Results

The distribution and solubility of chemical species of the complexes with and without EDTA or ISA were calculated using a MINEQL+ V5.0 program. The equilibrium constants collected at various ionic strengths were converted into equilibrium constants under the condition of $I=0$ by Davies eq[1,4].

2.1 Pu(IV)-EDTA System

Fig. 1 (a)~(c) is a graph showing speciation and solubility of a 10^{-3} M Pu(IV) ion in the 0, 10^{-6} , and 10^{-3} M EDTA containing aqueous solution.

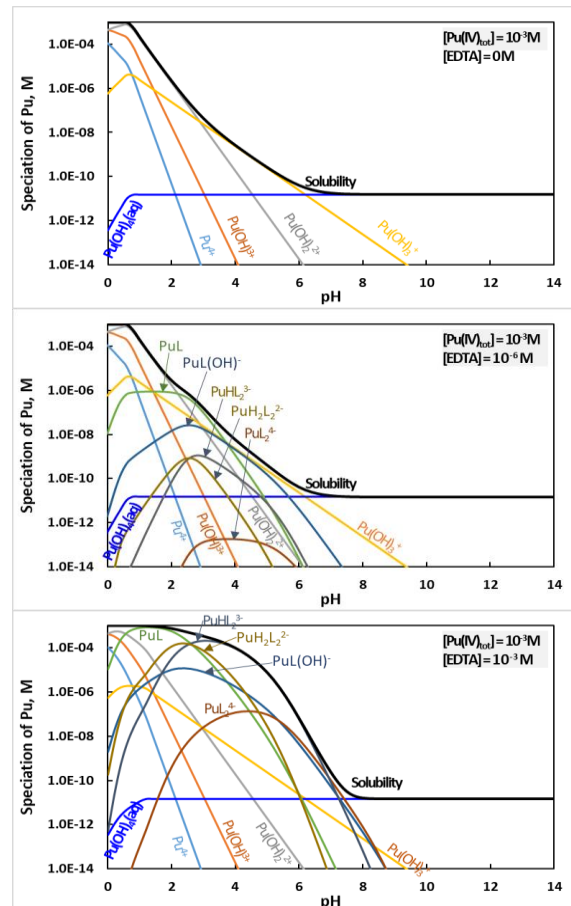


Fig. 1. Speciation of Pu(IV)-EDTA system at $I=0$ and 25°C in 10^{-3} M Pu(IV) and $[\text{EDTA}]=0$ M(a), 10^{-6} M(b), 10^{-3} M(c)

When the concentration of EDTA was 0, the Pu^{4+} , PuOH^{3+} , $\text{Pu}(\text{OH})_2^{2+}$, and $\text{Pu}(\text{OH})_3^+$ ions were distributed in an acid solution, and $\text{Pu}(\text{OH})_4(\text{aq})$ was only soluble in the alkaline region. Even if EDTA is added, the solubility of Pu(IV) is not affected because Pu(IV)-EDTA complex is not formed and only $\text{Pu}(\text{OH})_3(\text{aq})$ exists in the alkaline region ($\text{pH} > 8$). That is, it can be seen that EDTA in the pore water condition does not significantly affect on the solubility of Pu(IV).

2.2 Pu(IV)-ISA System

Fig.2 (a) - (c) are graphs showing the effect of ISA. Liquid chemical species other than hydrolysis products produced $\text{Pu}(\text{OH})_3(\text{ISA})\text{-H}^-$ and $\text{Pu}(\text{OH})_3(\text{ISA})\text{-2H}^{2-}$ ions. As the concentration of ISA increased, Pu(IV)-ISA Complexes had a significant effect on the solubility of Pu(IV) in alkaline conditions. Since the concentration of $\text{Pu}(\text{OH})_3(\text{ISA})\text{-2H}^{2-}$ ion increases in proportion to pH above pH 10, it is the chemical species that has the greatest influence on the solubility increase in the pore water region.

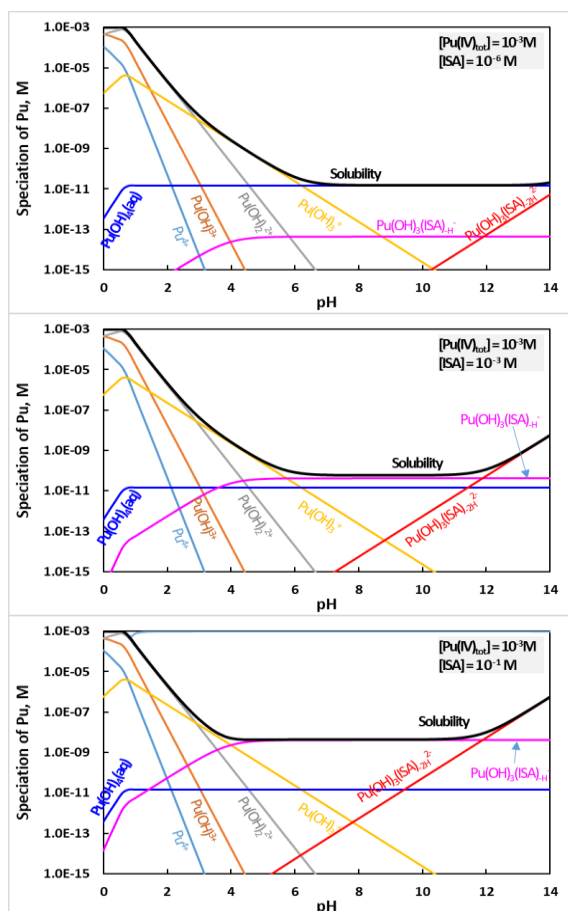


Fig. 2. Speciation of Pu(IV)-ISA system at I=0 and 25°C in 10^{-3}M Pu(IV) and $[\text{ISA}] = 10^{-6}\text{M}$ (a), 10^{-3}M (b), 10^{-1}M (c)

2.3 Pu(IV)-EDTA-ISA System

Fig.3 is a graph showing the effect of EDTA and ISA on the solubility curve of Pu(IV). It can be seen that the concentration of ISA affecting the solubility of Pu(IV) in the pore water region is $10^{-5} - 10^{-4}\text{M}$.

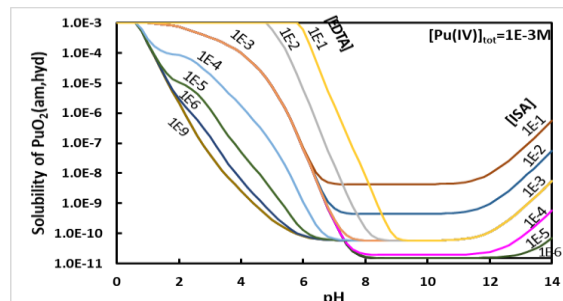


Fig. 3. Effect of $[\text{ISA}]$ and $[\text{EDTA}]$ on the solubility of Pu(IV)-ISA-EDTA system at I=0 and 25°C in 10^{-3}M Pu(IV) aqueous solution

3. Conclusions

The solubility of Pu(IV) and distribution characteristics of Pu(IV)-EDTA or Pu(IV)-ISA complexes was calculated by MINEQL program. In a strong alkaline atmosphere, which is a condition of repository pore water, ISA has a greater effect on the solubility of Pu(IV) ions than EDTA. Therefore, it is necessary to reduce the cellulose concentration in the waste drum as much as possible. The critical concentration of ISA was estimated to be about $10^{-5} - 10^{-4}\text{M}$.

REFERENCES

- [1] W.K. Choi et al., Characterization and Quantification Methodology of Organic Complexing Agents Generated by Radioactive Wastes from Nuclear Facilities and Radwaste Repository, KAERI/TR-9055/2021
- [2] D. Rai and A. Kitamura, Evaluation of equilibrium constants for deprotonation and lactonisation of α -D-isosaccharinic acid, J. Nucl. Sci. and Tech., 53, 4, 459-467, 2016
- [3] V. Neck, et al, Solubility of plutonium hydroxides/hydrous oxides under reducing conditions and in the presence of oxygen, Compt.Rendus Chem., 10, 959-977, 2007
- [4] W.D. Schecher, and D.C. McAvoy, MINEQL+ A Chemical Equilibrium Modeling System Version 5.0 for Windows User's Manual, ERA Hallowell, ME, 2015

Acknowledgements

This research was supported by Energy Technology Development Program through the Korea Institute of Energy Technology Evaluation and Planning (KETEP) funded by Ministry of Trade, Industry and Energy (No. 20203210100370)