

Formation of Pu(III) colloids observed by laser-induced breakdown detection

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1. Introduction

Plutonium chemistry in aquatic solutions is important to assess the safety of high-level radioactive waste disposals in a deep geological system with respect to isolation and immobilization of radioactive elements. Under environmental conditions plutonium can coexist in several different oxidation states: Pu(III), Pu(IV), Pu(V) and Pu(VI), which show drastically different chemical behaviors. The thermodynamic data of plutonium has been critically discussed in OECD/NEA-TDB reviews [1], but it is still difficult to ascertain reliable predictions of the total concentration of dissolved plutonium species under geochemical conditions of radioactive waste repositories. There have been several investigations on the solubility of plutonium hydroxide in the presence of reducing agents such as 50 bar H₂ [2], Na₂S₂O₄ [3], hydroquinone, and FeCl₂ [4]. In these studies, higher concentrations of dissolved plutonium species than the concentration predicted from the solubility product of Pu(IV) hydroxide were reported owing to the dominant oxidation state of Pu(III) in a solution. However, only one study [5] providing experimental solubility products for Pu(III) hydroxide as equilibrium solid phase was reported.

In the present work, the reduction conditions were controlled through electrolysis. An electrochemical cell with a Teflon vessel and quartz tubes containing electrodes were installed in a glove-box purged with Ar gas to prepare plutonium samples at different pHs under reducing condition. The concentration of hydrogen ions (H⁺) of plutonium solutions was reduced using an electric current from a Ag/AgCl reference electrode to a Pt working electrode, which called coulometric pH titration. The electrolytic reducing condition maintains the dominant oxidation state of Pu(III). Soluble species were investigated using absorption spectroscopy adopting a liquid waveguide capillary cell (LWCC) which has an optical path length of 100 cm. The formation of plutonium hydroxide colloids and solubility were determined by laser-induced breakdown detection (LIBD).

2. Methods and Results

2.1 Sample preparation

Pu(VI) stock solution in 1 mM HClO₄ was prepared by dissolution of PuO₂ (ORNL, isotopic composition:

99.932% ²⁴²Pu) as described in the previous report [6]. An aliquot of Pu(VI) solution was appropriately diluted with a high acidic solution (0.25 M HClO₄) and reduced to Pu(III) by electrolysis. The concentration of plutonium was 1.25 mM determined using liquid scintillation counting (LSC, TriCarb 2500 TR/AB, Packard).

The initial sample of Pu(III) to investigate formation of Pu(III) hydroxide colloids was prepared by dilution of Pu(III) stock solution in 0.1 M NaClO₄. The concentration of hydrogen ions (H⁺) was decreased by electrolysis without the addition of alkaline solution. During the coulometric pH titration, the concentration of plutonium and the oxidation state of Pu(III) were maintained. For example, 20 mL of Pu(III) sample at Pu concentration of 0.1 mM and pH 2 in 0.1 M NaClO₄ was prepared in a Teflon reactor. The current of 10 μA reduces H⁺ ions concentration of 18 μM per hour.

2.2 Measurements of pH and E_h

H⁺ ions concentrations were measured in small aliquots of samples with a combination glass electrode (Ross type, Orion) calibrated with pH buffers (pH 2.00, 4.01, 7.00 and 10.01, Orion). Redox potentials were measured with a Pt electrode (home-made with Pt wire) and a Ag/AgCl reference electrode (RE-5B, BASi, USA) calibrated with commercial redox buffers (470 and 640 mV, Schott Ins. GmbH, Germany).

2.3 Laser-induced breakdown detection (LIBD)

The formation of colloids in plutonium samples was monitored using LIBD. The second harmonic of the pulsed Nd:YAG laser (Surelite II, Continuum) was used as a light source. Laser-induced breakdown was optically detected by using a CCD camera (IMB-17FT, imi tech, Korea). The experimental setup was described elsewhere in detail [7]. The solubility limit of plutonium hydroxide was determined from the initial colloid formation in solutions.

2.4 UV-Vis absorption spectroscopy

Absorption spectra of soluble plutonium species were measured by using spectrophotometer (Cary5, Varian, Germany) with a sealable quartz cell (Macro117.100F, Hellma) or a LWCC (LWCC-3100, WPI, USA).

2.5 Results and discussion

Figure 1 shows absorption spectra of Pu samples at different pHs of 5.07 to 6.19 in the wavelength range of 400 to 700 nm. Absorbance of Pu(III) was decreased as the increase of pH without changes of peak positions in absorption spectrum for Pu³⁺ ions in a high acidic solution. The concentrations of Pu in the supernatant of samples determined using LSC were decrease from 0.076 mM at pH 5.07 to 0.033 mM at pH 6.19. The concentrations of soluble Pu(IV) were below the limit of detection (< 0.1 μM) of absorbance measurement at 470 nm using a LWCC with an optical path length of 100 cm.

Figure 2 (left) shows the breakdown (BD) probability as a function of laser pulse energy, which called as “s-curve”, for the same samples represented in Fig. 1. The black symbols indicate the s-curve for background material of 0.1 M NaClO₄ being similar compared with that for pure water (Element, Millipore Co., data are not shown). It means that there are no measurable colloids in the background materials using LIBD, by which polystyrene reference nanoparticles of small size (20 nm) in a very dilute concentration (< sub ng/mL) can be detected [7]. BD probabilities for plutonium samples at pH 5.07 and 5.51 were higher than those of 0.1 M NaClO₄ solution at the same laser pulse energy. The similar BD probabilities were observed for the initial plutonium sample at pH 3 which might be contaminated during preparation. It is speculated that these colloids are not Pu(III) hydroxide colloids. BD probabilities and absorbance in shorter wavelengths of the samples at pH 5.85 and 6.19 were increased. It indicates that the limit of solubility exceeded and Pu(III) hydroxide nanoparticles formed in a solution. The BD probabilities measured at the same laser pulse energy as a function of pH were also shown in Fig. 2 (right). The solubility product of plutonium hydroxide determined with absorption spectra and LIBD data will be discussed in comparison with the previous results [2, 5].

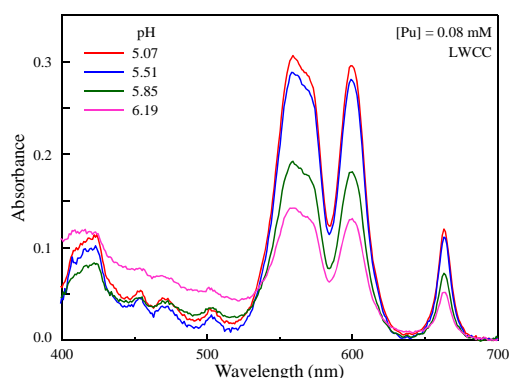


Fig. 1. Absorption spectra of plutonium solutions at various pHs measured using a LWCC in wavelength range of 400 to 700 nm. The concentration of plutonium was 0.08 mM in 0.1 M NaClO₄.

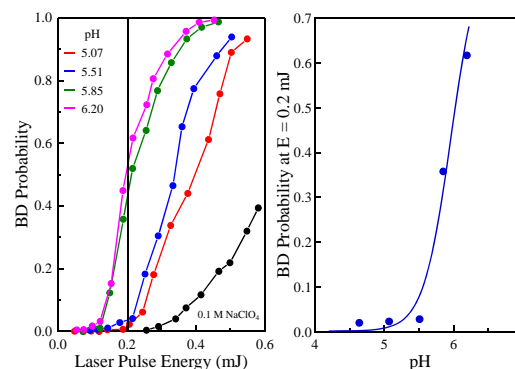


Fig. 2. BD probability of plutonium samples ([Pu] = 0.08 mM) measured as a function of laser pulse energy (left) and as a function of pH at the laser pulse energy of 0.2 mJ (right).

3. Conclusions

Electrolytic reduction was a useful method to investigate the hydrolysis, colloid formation and solubility of Pu(III) hydroxide. The oxidation state of Pu(III) maintained well during the reduction of hydrogen ions being comparable to strong reducing agents such as Fe powder. The determined solubility product was lower than the reported data by Felmy et al. [5]. The existence of Pu(IV), which can result in lower solubility investigated by measurement of redox potentials of samples will be presented in detail.

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REFERENCES

- [1] R. J. Lemire, J. Fuger, H. Mitsche, P. Potter, M. H. Rand, J. Rydberg, K. Spahiu, J. C. Sullivan, W. J. Ullman, P. Vitorge, H. Wanner, Chemical Thermodynamics Vol. 4, Chemical Thermodynamics of Neptunium and Plutonium. Elsevier, North-Holland, Amsterdam, 2001.
- [2] H. Nilsson, Y. Albinsson, G. Skarnemark, Dissolution of Plutonium(III) Hydroxide at 50 bar H₂, Mat. Res. Soc. Symp. Proc., Vol. 807, pp. 615-620, 2004.
- [3] K. Fujiwara, H. Yamana, T. Fujii, H. Moriyama, Solubility Product of Plutonium Hydrous Oxide and Its Ionic Strength Dependence, Radiochimica Acta, Vol. 90, pp. 857-861, 2002.
- [4] D. Rai, Y.A. Gorby, J. K. Fredrickson, D. A. Moore, M. Yui, Reductive Dissolution of PuO₂(am): The Effect of Fe(II) and Hydroquinone, J. Sol. Chem. Vol. 31, pp. 433-453, 2002.
- [5] A. R. Felmy, D. Rai, J. A. Schramke, J. L. Ryan, The Solubility of Plutonium Hydroxide in Dilute Solution and in High-Ionic-Strength Chloride Brines, Radiochimica Acta, Vol. 48, pp. 29-35, 1989.
- [6] H.-R. Cho, W. Cha, E. C. Jung, K. Song, Spectroscopic Speciation of Plutonium Reduced by Electrolysis, Transaction of the Korean Nuclear Society Spring Meeting, 2014.
- [7] E. C. Jung, H.-R. Cho, Characteristics of the Laser-Induced Breakdown Detection of Colloidal Nanoparticles for Determining Particle Size in the Delivery of Nanoparticles, ed. A. A. Hashim, InTech, Ch. 20, pp. 431-452, 2012.