

Spectroscopic Speciation of Plutonium Reduced by Electrolysis

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1. Introduction

Actinides chemistry, especially, on the plutonium in aquatic solutions is important to assess the safety of high-level radioactive waste disposals in a deep geological system. The isolation and immobilization of radionuclides are controlled by several chemical reactions such as solubility, complexation, sorption, colloid formation, and precipitation [1]. Plutonium can easily coexist in solutions as different oxidation species: Pu(III), Pu(IV), Pu(V) and Pu(VI). The oxidation state of plutonium should be carefully controlled to understand the chemical behaviors of plutonium. Pu(III) is not stable in aqueous solutions and easily oxidized in the atmosphere. In deep geological environments excluded oxygen, reducing condition is expected and will lead to rather stable Pu(III), which is very soluble compared to Pu(IV). Pu(III) ions are expected to form hydrolysis complexes in neutral and basic solutions similar to Am(III), Cm(III) and Eu(III). The reported formation constants of $\text{Pu}(\text{OH})_n^{3-n}$ ($n=1-4$) had been critically discussed, and only the first hydrolysis constant ($\log^* \beta_{11}^0 = -6.9 \pm 0.3$) was selected in a review [2]. The main reason for the large discrepancy of the formation constants for $\text{Pu}(\text{OH})_n^{3-n}$ ($n=2-4$) is the high tendency of oxidation of Pu(III).

In the present study, the reduction condition of Pu(III) was controlled by electrolysis. The electrolysis reactor was specially designed to investigate hydrolysis, colloid formation, and solubility of Pu(III) at different pHs. Pu(III) was reduced from higher oxidation states at acidic conditions, and the H^+ ion concentration in solutions was simultaneously decreased without the addition of alkaline solution by electrolysis. The soluble species was investigated using spectrophotometry adopting a capillary cell (LWCC, Liquid Waveguide Capillary Cell, WPI) and the formation of plutonium colloid and solubility was determined using LIBD (Laser Induced Breakdown Detection).

2. Methods and Results

2.1 Experimental

Pu stock solution was prepared by dissolution of PuO_2 (ORNL, isotopic composition: 99.932% ^{242}Pu) as described in the previous paper [3]. A trace amount of ^{241}Am generated by β -decay of ^{241}Pu (initial 0.035% of Pu) was removed using an anion-exchange resin (Biorad AG1-X8, 100-200 mesh) in a HCl medium. After the purification, the amount of americium can be

neglected and the activity of ^{242}Pu is about 86.5% of the total activity. The background material was converted into HClO_4 by repeatedly fuming in concentrate HClO_4 , and during this process Pu was oxidized into Pu(VI). The concentration of a Pu stock solution was 12.2 mM in 1 mM HClO_4 determined using liquid scintillation counting (LSC, TriCarb 2500 TR/AB, Packard).

To prepare Pu(III) samples, an aliquot of Pu(VI) solution was appropriately diluted with weak acidic NaClO_4 (0.1 M) and reduced to Pu(III) by electrolysis. Figure 1 (right) shows the electrolysis reactor (material: Teflon), which contains a Pu sample and a working electrode (Pt). Two separated quartz cells (left) which contain the counter electrode (Pt) and the reference electrode (Ag/AgCl), respectively, in 0.1 M NaClO_4 were installed in the Teflon reactor. pH_c ($-\log[\text{H}^+]$) was controlled with a current range of 1-20 μA . The current of 10 μA reduces 1×10^{-10} mole of H^+ ions per second. The pH was measured with a combination glass electrode (Ross type, Orion) calibrated with pH buffers (pH 2.00, 4.01, 7.00 and 10.01, Orion). After pH increase, the current was turned off for 1 hour to attain equilibration prior to absorption spectra and LIBD measurements in a sealable quartz cell (Macro 117.100F, Hellma) or a capillary cell.

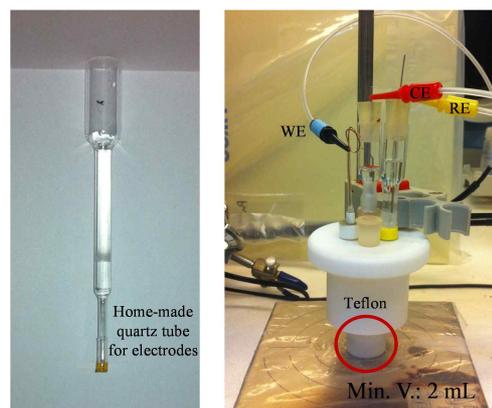


Fig. 1. Experimental setup.

LIBD is a laser-based method, being capable of quantifying aqueous nanoparticles of smaller sizes (< 100 nm) in a very dilute concentration. The principle and experimental setup of LIBD are described elsewhere in detail [4]. Absorption spectra of plutonium were measured by using a LWCC with an optical path length of 100 cm installed in a glove box and coupled with a spectrophotometer (Cary5, Varian) as described elsewhere in detail [3].

2.2 Absorption spectra of Pu(III)

Figure 2 shows the absorption spectra of a Pu(III) stock solution in the wavelength range of 450-700 nm during a reduction process. 2 mL of plutonium solution was prepared by dilution of Pu(VI) stock solution in 5 mM HClO₄. The concentration determined by LSC measurement was 0.16 mM. At the beginning of the reduction, the oxidation states of plutonium were mixed with Pu(III) and Pu(V). Pu(V) decreased and Pu(III) increased with the reduction time. Plutonium under a weak acidic condition was slowly reduced compared to that under a strong acidic condition. For example, 1 mM of Pu(VI) solutions in 1 M HClO₄ was reduced in 4 hours above -0.2 V (data not shown). The reduction potential from Pu(IV) to Pu(III) decreases with an increase of pH.

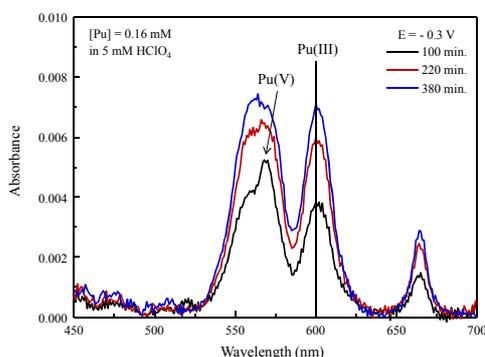


Fig. 2. Absorption spectra of plutonium during a reduction process in weak acidic condition by electrolysis. All plutonium was reduced to Pu(III) in 6 hours.

Figure 3 shows the absorption spectra of Pu(III) standard solution in the wavelength range of 450–850 nm measured using a LWCC (blue line) and a standard quartz cell (black line). The concentration of plutonium is 0.12 mM and the background material is 1 M HClO₄. Both spectra show the characteristic peaks of Pu(III) previously reported by Cohen [5]. The better S/N ratio of the absorption spectrum was obtained for a capillary cell compared with a standard quartz cell, as expected. Based on the Beer-Lambert law ($A = \epsilon cl$, where A is absorbance, ϵ is molar absorption coefficient [$M^{-1}cm^{-1}$], c is molar concentration [M], and l is an optical path length [cm]), the absorbance increased simply 100 times for a capillary cell due to the increase of the optical path length from 1 to 100 cm. In order to obtain calibration curves for the concentration measurement of Pu³⁺ ions by using a capillary cell, the absorption spectra were measured for several standard solutions having different concentrations in the range of 0.8–120 μM . The calibration curve shows good linearity between the absorbance at 601 nm and the concentration with a correlation coefficient of better than 0.99 (data not shown). The molar absorption coefficient for Pu³⁺ ions determined from the slope of the calibration curve was $32.9 \pm 0.1 M^{-1}cm^{-1}$ at 601 nm. The limit of detection for Pu³⁺ ions was 0.16 μM (3σ).

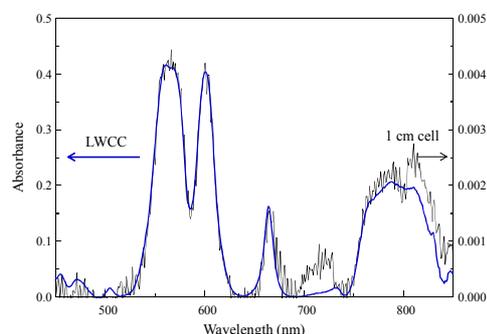


Fig. 3. Absorption spectra of Pu(III) in 1 M HClO₄ (pH 0) measured by using a LWCC (blue line) and a standard quartz cell (black line). At the concentration of 0.123 mM, the absorbance increased 100 times for a LWCC due to the increase of the optical path length of 1 to 100 cm.

3. Conclusions

In this study, an electrolysis system for the reduction of plutonium and H⁺ ions in a solution with small volume (> 2 mL) was installed in a glove box to investigate the hydrolysis, colloid formation and solubility of Pu(III) under a reducing condition. Pu(III) was reduced from the mixed plutonium oxidation states without the generation of Pu(IV) colloidal particles or precipitates under weak acidic conditions. A coulometric titration method was applied to adjust the pH without the addition of NaOH. The change of absorption spectra of Pu(III) and colloidal formation of plutonium with an increase of pH will be presented in detail.

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