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Influence of ethylenediaminetetraacetic acid on the long-term oxidation state distribution of plutonium

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HIGHLIGHTS

- Pu(V)-EDTA exhibits unique absorption bands at 571, 993, 1105, and 1150 nm.
- Pu(V)-EDTA spectrophotometry as a function of [EDTA] indicates formation of only 1:1 complexes.
- EDTA increases the rate of Pu(V/VI) reduction to stable Pu(IV)-EDTA complex(es).
- Pu(III) can persist much longer than expected in the presence of EDTA (110 days).

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ABSTRACT

Spectrophotometry was used to study the effect of EDTA on plutonium oxidation state distribution as a function of time, pH, and ligand-to-metal ratio (L/M) under anoxic conditions. Novel Pu(V)-EDTA absorption bands were identified at 571, 993, 1105, and 1150 nm with molar absorption coefficients of 15 ± 1, 6 ± 1, 10 ± 1, and 10 ± 1 $cm^{-1}M^{-1}$, respectively. Pu(V)-EDTA spectral changes occurred at L/M < 1, indicating only $Pu^{V}O_2(EDTA)^{3-}$ formed with $\log K = 3.6 \pm 0.3$. Time-resolved experiments showed EDTA drastically increased the Pu(V/VI) reduction rate, which we propose is driven by amine lone-pair electron donation and the oxidative decarboxylation of EDTA. Oxidation of Pu(III)-EDTA to Pu(IV)-EDTA occurred on a slower time scale (110–237 days) than previously reported (<15 min) and is hypothesized to be radiolysis driven. Pu(V/VI)-EDTA and Pu(III)-EDTA both approached Pu(IV)-EDTA stabilization over time, yet Pu(V/VI)-EDTA solubility data was ≥ 1.0 $\log_{10}$ units higher than predicted by Pu(IV)-EDTA solubility models, indicating that current thermodynamic models are incomplete. Ultimately, the data show EDTA preferentially stabilizes Pu(IV) over time regardless of initial oxidation state, but Pu(V)-EDTA can persist under environmentally-relevant conditions, emphasizing the need to continue investigating redox reactions, speciation, and behavior of these complexes to support the transuranic waste disposal and surface remediation/containment efforts.

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1. Introduction

To effectively protect human health and the environment, it is necessary to understand the geochemical behavior of plutonium. Specific environmental settings highlighting the need to understand the mobility of plutonium include the currently-operating deep geologic repository in the United States (i.e., the Waste Isolation Pilot Plant in Carlsbad, New Mexico) and near-surface systems where contamination is present because of nuclear weapons testing, improper storage or disposal, and aging infrastructure. Deep geologic repositories are expected to be anoxic, reducing, and alkaline, while near-surface systems can exhibit a wide range of redox environments. Therefore, there is a need to understand the stability of individual plutonium oxidation states and their interactions with other waste components under conditions that encompass the large variability of environmental systems.

Our work focuses on ethylenediaminetetraacetic acid (EDTA)

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interactions with plutonium. EDTA is used in defense production of plutonium and in the processing of plutonium-containing wastes as a decontamination and separations agent (Ayres, 1970; McFadden, 1980; Rai et al., 2008). It is co-disposed with plutonium in many waste streams, and plutonium-containing EDTA wastes have been inadvertently released into the environment (Freeman-Pollard et al., 1994; Rai et al., 2008).

Pu-EDTA systems encompass all four environmentally-relevant plutonium oxidation states (i.e., III–VI) (Clark et al., 2010; Kersting, 2013) and have been studied since the late 1950s (AlMahamid et al., 1996; Boukhalfa et al., 2004; Cauchetier and Guichard, 1975; 1973; Foreman and Smith, 1957a; 1957b; Gel'man et al., 1959; Merciny et al., 1978, Meyer et al., 2007; Mikhailov, 1969; Moskvin and Artyukhin, 1959; Poczynajl·o, 1991; 1989; Rai et al., 2010; 2008; 2001; Stepanov and Makarova, 1965; Thakur et al., 2009). The most attention has been paid to the aqueous-phase speciation of Pu(IV)-EDTA (AlMahamid et al., 1996; Boukhalfa et al., 2004; Cauchetier and Guichard, 1973; Foreman and Smith, 1957a, 1957b; Meyer et al., 2007; Mikhailov, 1969; Rai et al, 2001, 2008; Thakur et al., 2009), yet a critical review by the Nuclear Energy Agency does not select any Pu(IV)-EDTA complex(es) for inclusion in its Thermochemical Database (NEA-TDB) (Hummel et al., 2005). Recent studies interrogate Pu(IV)-EDTA over a large pH range ($0 \leq$ pH ≤ 13.5), generating three distinct speciation models (Boukhalfa et al., 2004; Meyer et al., 2007; Rai et al., 2008). Disagreements regarding speciation are compounded by inconsistencies in Pu(IV)-EDTA complex formation constants, which can vary among single species by up to 20 orders of magnitude (e.g., $Pu(OH)(EDTA)^-$, Table A1). Thus, even with advances in technology and multiple systematic studies investigating Pu(IV)-EDTA interactions over the last 60 years, the aqueous-phase speciation of Pu(IV)-EDTA remains unclear.

The redox behavior of plutonium in the presence of EDTA is one of the least investigated, but most important, aspects of Pu-EDTA systems. Pu(VI) reduction to Pu(V) and Pu(IV) in the presence of EDTA has been observed under acidic conditions (pH 3–6.5), showing that the reduction to Pu(V) is practically instantaneous while further reduction to Pu(IV) is markedly slower (AlMahamid et al., 1996; Cauchetier and Guichard, 1975; Foreman and Smith, 1957b; Kabanova et al., 1960; Reed et al., 1998). There is general consensus that one molecule of EDTA can reduce six Pu(VI) atoms and that the reduction rate is pH dependent (AlMahamid et al., 1996; Cauchetier and Guichard, 1975; Kabanova et al., 1960). However, it remains unclear whether Pu(IV) is the stable reduction product at all pH values—further reduction to Pu(III) or stabilization as Pu(V) may occur—and the mechanism of reduction has not been defined.

Pu(III) also exhibits redox changes in the presence of EDTA. Multiple studies under acidic conditions (i.e., pH ≤ 4.6) show that Pu(III) is completely oxidized to Pu(IV)-EDTA within 15 minutes, but that the oxidation rate decreases with increasing pH (AlMahamid et al., 1996; Boukhalfa et al., 2004; Cauchetier and Guichard, 1973; Foreman and Smith, 1957a). This rapid oxidation is attributed to the greater thermodynamic stability of Pu(IV)-EDTA complex(es) with respect to Pu(III)-EDTA. However, little research has been dedicated to understanding the long-term behavior of Pu(III)-EDTA under alkaline conditions and the mechanism for the rapid Pu(III) oxidation observed in the presence of EDTA is not yet explained.

In the present study, we examine the long-term ($t \leq 616$ days) redox behavior of Pu(III)- and Pu(V/VI)-EDTA systems under anoxic, circumneutral to alkaline conditions. This is coupled with further interrogation of Pu(III)- and Pu(V)-EDTA spectrophotometry for additional analytical identification and quantification of Pu-EDTA complexes. Finally, we compare our experimental results to current thermodynamic models in order to resolve the literature contradictions described above.

2. Materials and methods

2.1. Anoxic atmosphere

All experimental solutions were prepared with Milli-Q water (18.2 MΩ•cm) that was boiled for at least 1 h while being purged with nitrogen gas. Experiments were performed under nitrogen atmosphere (<1 ppm O_2, (23 ± 2)°C). Nitrogen atmosphere was maintained in MBraun gloveboxes with integrated recirculating gas purifier units certified to maintain $O_2(g)$ and $H_2O(g) < 1$ ppm ("MBraun Operating Manual," 2014). $O_2(g)$ was constantly monitored throughout all experimentation. While occasional fluctuations occurred during glovebox use, $O_2(g)$ exposure was operationally minimized during sampling. Between active sampling points, bottles were sealed with Parafilm™ and stored in two-layer containment to prevent any potential oxygen contamination.

2.2. Oxidation state-specific Pu-EDTA spectrophotometry

Oxidation state-specific plutonium-EDTA spectrophotometry experiments were performed using weapons-grade ^{239}Pu. Isotopic distribution, descriptions of Pu(III), Pu(IV), and Pu(V) preparation procedures, and oxidation state distributions are provided in the Appendix. Aliquots of Pu(III) in 0.1 M HCl ($[Pu(III)]_T = (7.3 \pm 0.5) \times 10^{-5}$ M) were spiked into freshly-prepared EDTA solutions (0.0001–0.01 M) at acidic pH and progressively titrated to higher pH (2–10). At each pH, experimental solutions were analyzed with UV–Vis–NIR after an hour-long equilibration period. Due to the use of ^{239}Pu instead of ^{242}Pu, we were unable to eliminate some Pu(IV)-EDTA formation in these experiments ($\leq$ 24% oxidation within 1 h).

To verify Pu(IV)-EDTA spectrophotometry for Beer-Lambert law calculations, Pu(IV) in 0.1 M HCl ($[Pu(IV)]_T = (1.34 \pm 0.01) \times 10^{-4}$ M) was spiked into a freshly-prepared 1.01 ± 0.05 mM EDTA solution at pH 4 and analyzed with UV–Vis–NIR after equilibrating for three days. The resulting Pu(IV)-EDTA spectrum is provided in Fig. A1.

Pu(V) in 0.1 M PIPES/NaCl at pH 6.5 ± 0.1 was titrated with EDTA in 0.1 M PIPES/NaCl to vary ligand-to-metal ratio (L/M = 0–100, $[Pu(V)]_T = (2.33 \pm 0.08) \times 10^{-4}$ M). Each titrated solution equilibrated for ~15 minutes before pH and UV–Vis–NIR measurements. Longer equilibration times were not possible due to reduction to Pu(IV)-EDTA.

In our experiments, Pu(VI) was not stable in the presence of EDTA long enough to investigate the absorption spectrophotometry of the complex.

2.3. Time-resolved experiments

Time-resolved spectrophotometric experiments were performed using ^{242}Pu. Isotopic content, descriptions of Pu(III) and Pu(V/VI) stock preparation procedures, and oxidation state distributions are provided in the Appendix. Batch experiments were conducted with $[Pu(III)]_T = (1.01 \pm 0.03) \times 10^{-4}$ M at pH 4, 6, and 8 (±0.15) and $[Pu(V/VI)]_T = (4.33 \pm 0.02) \times 10^{-4}$ M at pH 4, 6, 8, and 10 (±0.15), 1.01 ± 0.05 mM EDTA, and constant ionic strength (I) = 0.10 ± 0.01 M Na_4EDTA-Na_2H_2EDTA-NaCl-HCl-NaOH. The quantity of NaCl needed to maintain constant I was calculated for each experimental pH. The pH of time-resolved experiments fluctuated over time and pH values were measured at regular intervals (Figs. A2–A3). Plutonium concentrations were determined by ICP-MS after ultrafiltration with 10 kD centrifugal filters (pore size ≈ 2–3 nm, Nanosep®, Pall Life Sciences). All time-resolved experiments were analyzed using UV–Vis–NIR before and after

ultrafiltration to assess the potential for colloid formation. No differences were observed between spectra of filtered and unfiltered samples containing EDTA, indicating no measurable colloidal species were present. Experiments were conducted over a range of short time points (26 minutes–6 days) and monitored periodically up to 616 days.

2.4. Analytical methods

Absorption spectra were collected on a Varian Cary 5000 UV–Vis–NIR spectrophotometer from 350 to 1100 nm with a scan rate of 60 nm min^{-1} and a 1-cm path length in anoxically-sealed quartz cuvettes. The spectrophotometer was regularly checked against NIST certified optical density and wavelength standards to confirm instrument calibration. Samples were analyzed with a 0.1 M NaCl background correction. Molar extinction coefficients were calculated using the Beer-Lambert law (see Appendix). Uncertainties in molar extinction coefficients were calculated through error propagation using measurement uncertainties of 0.0002 A.U. for absorbance, 0.5 nm for wavelength, and %RSD values for ICP-MS concentrations.

An Agilent 7900 quadrupole ICP-MS was used to determine aqueous plutonium concentrations. ICP-MS samples were prepared in 2–5% nitric acid and analyzed with an indium internal standard to monitor for instrumental drift and matrix effects. External calibration with NIST traceable standards (Eckert and Ziegler) was used to determine unknown elemental plutonium concentrations. Concentration data at each sampling point is tabulated in the Appendix.

All pH measurements were performed using an Orion 3 Star portable pH meter and a semimicro Ross combination pH electrode calibrated with standard buffer solutions (pH 4–10, Fisher certified). Redox potential was measured using an Orion portable ORP meter and a micro Mettler Toledo combination oxidation-reduction potential glass electrode. Measured potentials were converted to E_h through a standard correction for the potential of the inner-reference electrode with 3 M KCl at 22 °C (+207 mV) and further converted to pe (pe = -log $a_e^- = 16.9*E_h(V)$). Redox measurements equilibrated for a minimum of 15 min until the drift of the electrode was observed to be $\leq$ 3.0 mV min^{-1}.

3. Results and discussion

3.1. Oxidation state-specific Pu-EDTA spectrophotometry

We used UV–Vis–NIR to determine the effect of EDTA complexation on oxidation state-specific plutonium spectra. Molar extinction coefficients (ε) were calculated from UV–Vis–NIR and ICP-MS results and compared to literature-based values and speciation assignments (Table 1). When literature speciation information was contradictory, we considered ε to be apparent, as opposed to absolute. New absorption bands were identified for Pu(III)-EDTA and Pu(V)-EDTA complexes with ε values ranging from 2 ± 1 to 33 ± 4 $cm^{-1}M^{-1}$ depending upon ligand-to-metal ratio (L/M) and pH. Values for plutonium aquo ion spectra from this work and the literature are provided for verification of methodology and calculations.

3.1.1. Pu(III)-EDTA

The effect of EDTA and pH on the Pu(III) absorption spectrum was determined through pH titrations at three different ligand-to-metal ratios (L/M = 1, 10, and 100). Absorption exaltation occurred at 565, 965, and 1150 nm upon the addition of EDTA as compared to the spectrum of Pu(III) in 0.1 M HCl. Changes in intensity varied as a function of pH (Fig. 1a and b). At constant L/M = 1, increasing pH resulted in a systematic decrease in absorption at 565 nm and an increase in absorption at 965 and 1150 nm. Shifts were also observed: as pH increased from 2 to 10, the absorption band at 565 nm exhibited a 10-nm red shift and at pH $\geq$ 4, the wide 900 nm peak split into two separate peaks centered at approximately 885 and 905 nm. We attributed these systematic shifts with respect to pH to a transition between Pu^{III}(HEDTA) (aq) and $Pu^{III}(EDTA)^-$ with increasing alkalinity.

Varying L/M also caused changes within the Pu(III)-EDTA spectra. As L/M increased from 1 to 100, absorption exaltation occurred at 565 nm accompanied by red shifts at 565 and 601 nm (Fig. 1c). At higher wavelengths, increasing L/M caused a decrease in absorption and further splitting of the 900 nm peak. The 1150 nm peak decreased in intensity while the 1130 nm peak grew in with increasing L/M (Fig. 1d). These changes were less systematic compared to those observed as a function of pH, which we attribute to achieving 100% Pu(III)-EDTA complexation at L/M $\geq$ 1. Thus, they were an extension of changes observed upon initial addition of EDTA. A peak at 665 nm is observed in the spectrum of Pu(III) in 0.1 M HCl and in Pu(III)-EDTA systems regardless of pH (Fig. 1a). The Pu(III) aquo ion hydrolyzes with increasing pH, ultimately limiting the solubility of Pu(III) under alkaline conditions. Therefore, we suggest that the 665 nm peak in the spectrum of Pu(III) in the presence of EDTA at pH 10 (Fig. 1c) is due to the formation of a Pu(III)-EDTA complex with $\varepsilon = 12 \pm 1$ $cm^{-1}M^{-1}$. This molar extinction coefficient is lower than $\varepsilon_{Pu(III),aq} = 16$ $cm^{-1}M^{-1}$, suggesting that absorption at 665 nm is slightly decreased upon Pu(III)-EDTA complex formation. All subsequent Beer-Lambert law calculations for experiments in the presence of EDTA were conducted with $\varepsilon = 12 \pm 1$ $cm^{-1}M^{-1}$, since the Pu(III)-EDTA peak at 665 nm is least affected by L/M and pH changes.

3.1.2. Pu(V)-EDTA

The effect of EDTA on Pu(V) spectrophotometry was investigated through a series of EDTA titrations from L/M = 0–100 into a ^{239}Pu(V) solution at pH ~6.5 (held constant with 0.1 M PIPES). Each solution was analyzed within 15 min of titration to prevent reduction to Pu(IV)-EDTA. Fig. 2 shows UV–Vis–NIR spectra of Pu(V) as a function of L/M compared to the pure ^{239}Pu(V)/PIPES spectrum.

Many changes occurred in the Pu(V) spectra over the range L/M = 0.01–1, including peak shifts, peak splitting, and ingrowth of distinct Pu(V)-EDTA absorption bands (Fig. 2a). We observed a slight red shift and sharpening for all peaks between 500 and 600 nm (Fig. 2c). The sharp Pu(V) aquo ion peak at 569 nm gradually shifted to 571 nm and the full width at half max decreased by approximately one third. In the 700–900 nm region, the wide peaks at 770 and 840 nm each split, resulting in four absorption bands at 767, 775, 834, and 849 nm. Finally, the 950–1200 nm region of the spectrum showed new peak ingrowth (Fig. 2d). With increasing L/M, the intensity of the 1130 nm peak decreased while nearby peaks increased in intensity and split, yielding two distinct absorption bands at 1105 and 1150 nm.

The Pu(V)-EDTA spectrum remained constant at L/M $\geq$ 1, indicating the formation of only 1:1 Pu(V)-EDTA complex(es). Notably, we observed an isosbestic point between a Pu(V) aquo ion band at 999 nm and a Pu(V)-EDTA band at 993 nm (Fig. 2b). At pH = 6.5, we expect this 1:1 Pu(V)-EDTA complex to be in its unprotonated form (i.e., as $PuO_2(EDTA)^{3-}$) (Cauchetier and Guichard, 1975; Gel'man et al., 1959). From this isosbestic point, we calculated $\varepsilon = 6 \pm 1$ $cm^{-1}M^{-1}$ and an approximate $\log K(PuO_2(EDTA)^{3-}) = 3.6 \pm 0.3$ ($PuO_2^+ + EDTA^{4-} \leftrightarrow PuO_2(EDTA)^{3-}$), which is lower than described elsewhere, indicating a less stable complex than previously reported (Cauchetier and Guichard, 1975; Gel'man et al., 1959).

With the identification of novel Pu(V)-EDTA absorption bands at

Table 1
Absorption band maxima, molar extinction coefficients (ε), and species assignments for plutonium aquo ions and Pu-EDTA complexes.

Peak Identification	Absorption Maxima (nm)	Calculated ε ($cm^{-1}M^{-1}$)	Literature ε ($cm^{-1}M^{-1}$)	Aqueous Species
Pu(III)	601	31 ± 3	38[a]	Pu(III), pH 0
Pu(III)	665	12 ± 3	16[a]	Pu(III), pH 0
Pu(IV)	470	56 ± 3	56.5[a]	Pu(IV), pH 0
Pu(IV)	653	36 ± 3	35[a]	Pu(IV), pH 0
Pu(V)	569	19 ± 4	19[a]	Pu(V), pH 3.14
Pu(V)	770	–	–	Pu(V), pH 6.5, PIPES
Pu(V)	840	–	–	Pu(V), pH 6.5, PIPES
Pu(V)	999	2 ± 1	–	Pu(V), pH 6.5, PIPES
Pu(V)	1130	–	–	Pu(V), pH 6.5, PIPES
Pu(VI)	830	510 ± 31	555[a]	Pu(VI), pH 0
Pu(III)-EDTA	565	43 ± 4[†]	54[b]	Pu^{III}(HEDTA)(aq)
Pu(III)-EDTA	605[b]	28 ± 3[†]	–	Pu^{III}(HEDTA)(aq)
Pu(III)-EDTA	900[b]	10 ± 1[†]	–	Pu^{III}(HEDTA)(aq)
Pu(III)-EDTA	575	42 ± 5[‡]	60[c]	$Pu^{III}(EDTA)^-$
Pu(III)-EDTA	610[c]	33 ± 4[‡]	–	$Pu^{III}(EDTA)^-$
Pu(III)-EDTA	885[c]	6 ± 2[‡]	–	$Pu^{III}(EDTA)^-$
Pu(III)-EDTA	905[c]	8 ± 2[‡]	–	$Pu^{III}(EDTA)^-$
Pu(III)-EDTA	665	12 ± 1	–	–
Pu(III)-EDTA	965	–	–	–
Pu(III)-EDTA	1150	–	–	–
Pu(IV)-EDTA	453	37 ± 2*	45.7[e]	Pu^{IV}EDTA(aq)
			75.0[e]	$Pu^{IV}(EDTA)_2H^{3-}$
			50.2[e]	$Pu^{IV}(EDTA)_2H_2^{2-}$
Pu(IV)-EDTA	495	–	59.1[e]	Pu^{IV}EDTA(aq)
			47.1[e]	$Pu^{IV}(EDTA)_2H_2^{2-}$
Pu(IV)-EDTA	504	58 ± 2*	44.1[d]	–
			96[e]	$Pu^{IV}(EDTA)_2H^{3-}$
			55.0[e]	$Pu^{IV}(EDTA)_2H_2^{2-}$
			84[b]	Pu^{IV}EDTA(aq)
Pu(IV)-EDTA	655	–	–	–
Pu(V)-EDTA	555[f]	2 ± 1[⁂]	–	$Pu^{V}O_2(EDTA)^{3-}$
Pu(V)-EDTA	571[g]	15 ± 1[⁂]	–	$Pu^{V}O_2(EDTA)^{3-}$
Pu(V)-EDTA	767	–	–	$Pu^{V}O_2(EDTA)^{3-}$
Pu(V)-EDTA	775	–	–	$Pu^{V}O_2(EDTA)^{3-}$
Pu(V)-EDTA	834	–	–	$Pu^{V}O_2(EDTA)^{3-}$
Pu(V)-EDTA	849	–	–	$Pu^{V}O_2(EDTA)^{3-}$
Pu(V)-EDTA	993[g]	6 ± 1[⁂]	–	$Pu^{V}O_2(EDTA)^{3-}$
Pu(V)-EDTA	1105	10 ± 1[⁂]	–	$Pu^{V}O_2(EDTA)^{3-}$
Pu(V)-EDTA	1150	10 ± 1[⁂]	–	$Pu^{V}O_2(EDTA)^{3-}$
Pu(VI)-EDTA	843[g]	–	–	–

*Because we were unable to assign speciation to each complexation peak, the molar extinction coefficients calculated here should be taken as apparent, not absolute, values.
[†]Calculated for L/M = 10 at pH = 2.
[‡]Calculated for L/M = 10 at pH = 10.
[⁂]Calculated for L/M = 1–100 at pH 6.5.
[a] (Clark et al., 2010).
[b] (Cauchetier and Guichard, 1973) L/M = 8, pH ≤ 6.
[c] (Cauchetier and Guichard, 1973) L/M = 6, pH ≥ 6.
[d] (AlMahamid et al., 1996).
[e] (Meyer et al., 2007).
[f] (Reed et al., 1998).
[g] (Cauchetier and Guichard, 1975).

571, 993, 1105, and 1150 nm, we conclude that Pu(V)-EDTA spectrophotometry is a useful tool for future studies of Pu-EDTA complexation. The absorption band at 993 nm is clearly distinct from other absorption bands in plutonium aquo ion and EDTA complexation spectra, and thus can be utilized for Pu(V)-EDTA quantification without extensive spectral deconvolution. This peak was an integral part of our oxidation state determination in the time-resolved experiments described below.

3.2. Pu-EDTA oxidation state distribution experiments

We monitored plutonium oxidation state distribution changes in the presence of EDTA as a function of initial oxidation state, pH, and time. To minimize radiolytic effects on Pu-EDTA chemistry, these experiments were conducted with ^{242}Pu, which has a longer half-life than ^{239}Pu. We used Pu(III) and a mixture of Pu(V) and Pu(VI) (i.e., Pu(V/VI)) to represent the initial oxidation state distribution of both reducing and oxidizing environmental conditions, respectively, and completed additional experiments in 0.1 M NaCl for the Pu(V/VI) mixture to create a baseline for the rate of reduction in the absence of EDTA.

3.2.1. Spectrophotometry as a function of time

Absorption spectra were collected 26 min after addition of Pu(V/VI) to two experimental solutions—one containing 1 mM EDTA and another containing 0.1 M NaCl (Fig. A4). Pu(VI) peaks disappeared in the experiment containing EDTA and were replaced by the Pu(V)-EDTA peak at 571 nm, suggesting complete reduction of Pu(VI) to Pu(V)-EDTA within the 26-min reaction time. The control experiment without EDTA exhibited an oxidation state distribution identical to the stock. These spectral results confirm that the presence of EDTA facilitates the reduction of Pu(VI) to Pu(V)-EDTA,

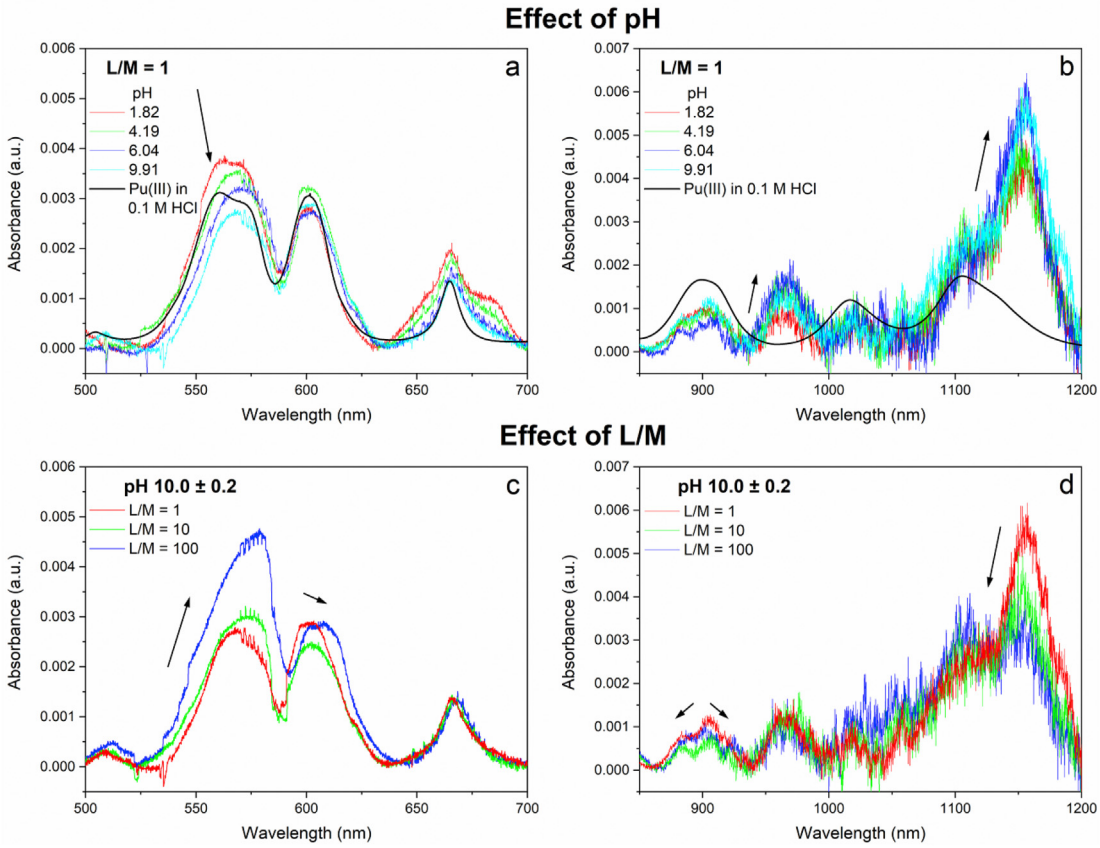


Fig. 1. UV–Vis–NIR absorption spectra of Pu(III) in 0.1 M HCl (Reed, 2020) and Pu(III)-EDTA showing the effect of pH (1.82–9.91) at constant L/M = 1 (top) and the effect of ligand-to-metal ratio (L/M = 0–100) at constant pH = 10 ± 0.2 (bottom). Spectra are normalized to equivalent plutonium concentration for comparison. Arrows highlight shifts, exaltation, or decreases in absorption as a function of L/M or pH.

consistent with literature.

UV–Vis–NIR spectra were collected as a function of time from 6 days to 616 days. We observed changes in the spectroscopy of Pu(V/VI) in 0.1 M NaCl, Pu(V/VI) in 1 mM EDTA, and Pu(III) in 1 mM EDTA (Fig. 3). For Pu(V/VI) in 0.1 M NaCl, the intensity of Pu(VI) absorption bands decreased over time. This was coupled with minor increases in Pu(V) absorption bands (not seen in Fig. 3a due to the comparatively large ε value for Pu(VI) aquo ion peaks) and an overall loss in total intensity (Fig. 3a). Theloss in absorption intensity is explained by an overall decrease in aqueous plutonium concentration; these data indicate the formation of aqueous Pu(V) and a precipitate over time. In contrast, no Pu(VI) absorption bands were observed in the spectra for Pu(V/VI) in 1 mM EDTA. Instead, Pu(V)-EDTA peaks at 571 and 993 nm decreased in intensity and Pu(IV)-EDTA peaks at 453 and 504 nm increased in intensity (Fig. 3b). For the Pu(III) in 1 mM EDTA system, Pu(III)-EDTA peaks at 605 and 665 nm were present from 6 to 110 days and accompanied by minor ingrowth of Pu(IV)-EDTA peaks (Fig. 3c). After 237 days, the Pu(III)-EDTA absorption bands were completely replaced by Pu(IV)-EDTA peaks at 453, 504, and 655 nm.

3.2.2. *Effect of pH*

Changing the pH of the system resulted in changes in the spectroscopy of Pu(V/VI) in 0.1 M NaCl and Pu(V/VI) in 1 mM EDTA. We observed only minor changes in the time-resolved UV–Vis–NIR spectra of Pu(V/VI) in 0.1 M NaCl as a function of pH. For example, there was a 25-nm red shift for the Pu(VI) absorption band at 830 nm as the pH increased from 4 to 10 (Fig. A5) due to the hydrolysis of plutonium (Reilly and Neu, 2006). In contrast, we observed a large pH dependence for the Pu(V/VI) in 1 mM EDTA system. In general, higher pH values stabilized higher oxidation states of plutonium. Although Pu(V/VI) reduction to Pu(IV) occurred across the pH range, the Pu(IV)-EDTA absorption bands (453, 504 nm) decreased in intensity with increasing pH. Simultaneously, the Pu(V)-EDTA peak (571 nm) increased in intensity with increasing pH (Fig. A6). Additionally, we observed a decrease in the aqueous plutonium concentration and the formation of a yellow-green precipitate at pH > 8.9. At pH $\geq$ 4, hydrolysis competes with Pu(IV)-EDTA complexation, resulting in less soluble plutonium hydroxide complexes (Rai et al., 2008). While the precipitate could not be characterized due to limited sample material, we suspect it is a Pu(IV)-hydroxide solid due to this competition. Unlike Pu(V/VI) experiments, the spectroscopy of Pu(III) in 1 mM EDTA showed no significant pH dependence with respect to the rate of Pu(III) oxidation (Fig. A7).

3.2.3. *Plutonium oxidation state distribution as a function of time*

The Beer-Lambert law (see Appendix) was used to determine plutonium oxidation state distributions as a function of time (Fig. 4). When comparing Pu(V/VI) in 0.1 M NaCl to Pu(V/VI) in 1 mM EDTA, it was apparent that, regardless of pH, the presence of EDTA increased the rate of plutonium reduction. After 6 days at pH $\approx$ 6, the NaCl experiment was approximately 10% Pu(VI) and 90% Pu(V) (Fig. 4a), whereas the EDTA experiment was approximately 50% Pu(V)-EDTA and 50% Pu(IV)-EDTA (Fig. 4b); after ~600 days, the NaCl experiment remained ~90% Pu(V) while the EDTA experiment was 100% Pu(IV)-EDTA. Similar observations were made at higher pH.

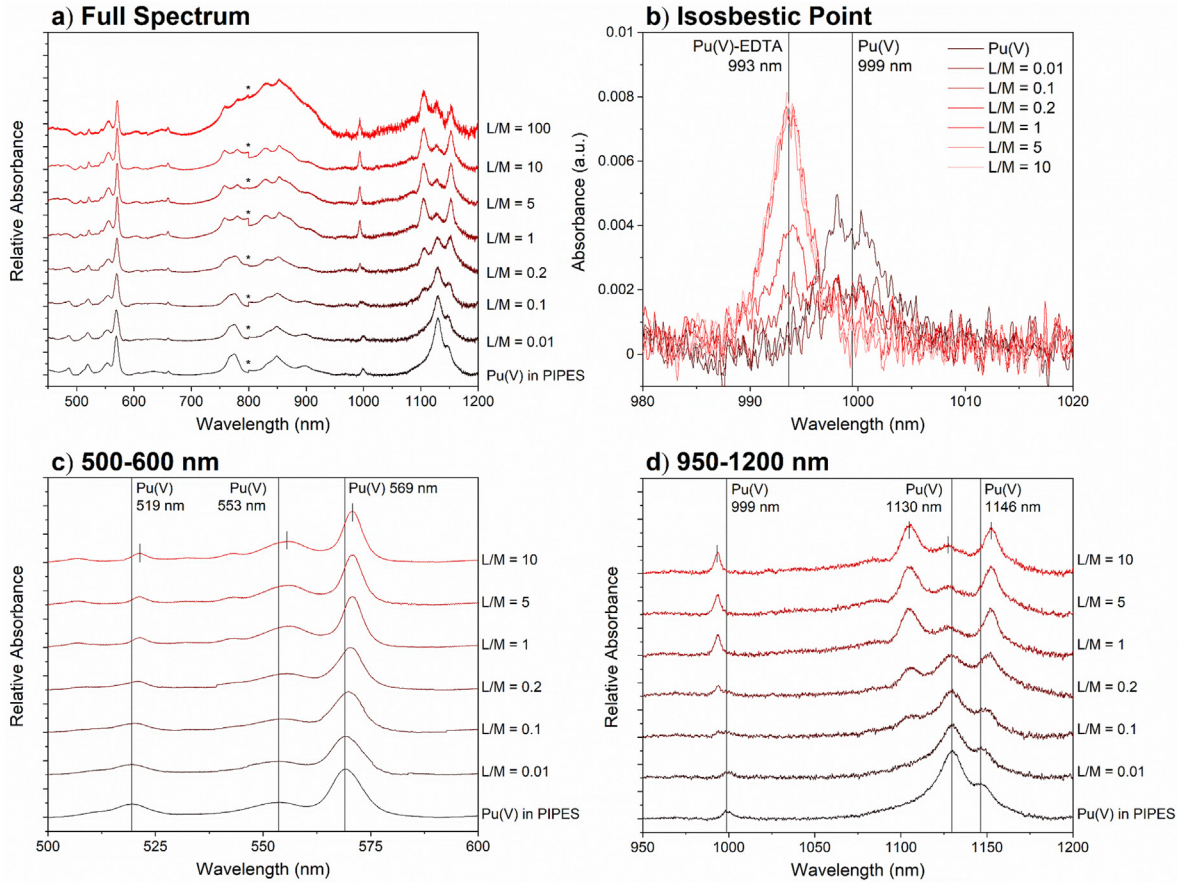


Fig. 2. UV–Vis–NIR absorption spectra of Pu(V)-EDTA at pH = 6.5 ± 0.1 as a function of ligand-to-metal ratio (L/M = 0–100) focused on (a) the full spectrum, (b) the isosbestic point between the Pu(V) aquo ion absorption band at 999 nm and the Pu(V)-EDTA absorption band at 993 nm, (c) peak shifts from 500 to 600 nm, and (d) peak shifts from 950 to 1200 nm. Solid lines represent the locations of Pu(V) aquo ion absorption bands before addition of EDTA. Stars signify an instrumental artifact caused by a detector/grating change.

The mechanism controlling Pu(V/VI) reduction by EDTA is unknown, but amine-bearing compounds, which have nitrogen lone-pair electron donors, and H_2O_2 produced during the alpha radiolysis of water are both capable of reducing plutonium (Barney, 1971, 1976; Koltunov et al., 1999; Maillard and Adnet, 2001; Morgenstern and Choppin, 1999; Morrison et al., 2018; Rabideau et al., 1958). The use of ^{242}Pu within this study resulted in minimal contributions from alpha radiolysis; a rough calculation (see Appendix) shows that insufficient H_2O_2 accumulated within 34 days to have caused the observed reduction to Pu(IV). A direct comparison to experiments without EDTA provides evidence that EDTA is the source of reduction; alpha radiolysis should occur similarly in both experiments, yet systems without EDTA reduced at a slower rate than systems with EDTA.

The literature reports many pathways for the oxidative breakdown of EDTA (Hanna et al, 1969, 1972, 1975; Ito et al., 1980; Johnson et al., 1972; Motekaitis et al., 1980; Sun et al., 1991). Based on these reported mechanisms, we hypothesize that the mechanism of plutonium reduction within our system may involve the oxidative decarboxylation of EDTA. Following complexation, the rapid reduction from Pu(VI)-EDTA to Pu(V)-EDTA occurs through a single-electron transfer from an amine lone-pair to the plutonium center of the complex (reaction 1, x = 0–4).

$$H_xEDTA^{-(4-x)} + PuO_2(EDTA)^{2-} \rightarrow H_xEDTA^{-(3-x)} + PuO_2(EDTA)^{3-} \quad (1)$$

The second reduction reaction (i.e., the reduction of Pu(V)-EDTA) proceeds through the oxidative decarboxylation of EDTA, which involves the breaking of strong axial ("yl") oxygen bonds within plutonyl (PuO_2^+) and the cleavage of a C–N bond within EDTA, resulting in a Pu(IV)-EDTA complex and ethylenediaminetriacetic acid (H_xED3A, x = 0–3). The breaking of both the "yl" and C–N bonds causes the second redox reaction to be slower relative to reaction 1. This second reaction can be written as reaction 2 under acidic conditions (pH ≈ 1.5–5). Reaction 2 also requires H^+, indicating that reduction to Pu(IV)-EDTA is favored under more acidic conditions; this is supported through our long-term experimental results (Fig. 4b).

$$H_xEDTA^{-(4-x)} + H^+ + PuO_2(EDTA)^{3-} \rightarrow H_xED3A^{-(4-x)} + CO_2 + HCHO + Pu(OH)(EDTA)^- \quad (2)$$

The literature provides definitive support for the oxidative decarboxylation of EDTA under similar experimental conditions (Hanna et al, 1969, 1972, 1975; Ito et al., 1980; Johnson et al., 1972; Motekaitis et al., 1980; Sun et al., 1991). This oxidative breakdown mechanism is possible under our experimental conditions because there was an excess of EDTA. If oxidative breakdown occurred as a result of reduction, enough EDTA remained in solution to fully complex all aqueous plutonium.

Pu(III) in 1 mM EDTA exhibited ≤ 24% oxidation to Pu(IV)-EDTA within 110 days (Fig. 4c). In later time points, complete oxidation to Pu(IV)-EDTA complex(es) was observed. Our observations contrast

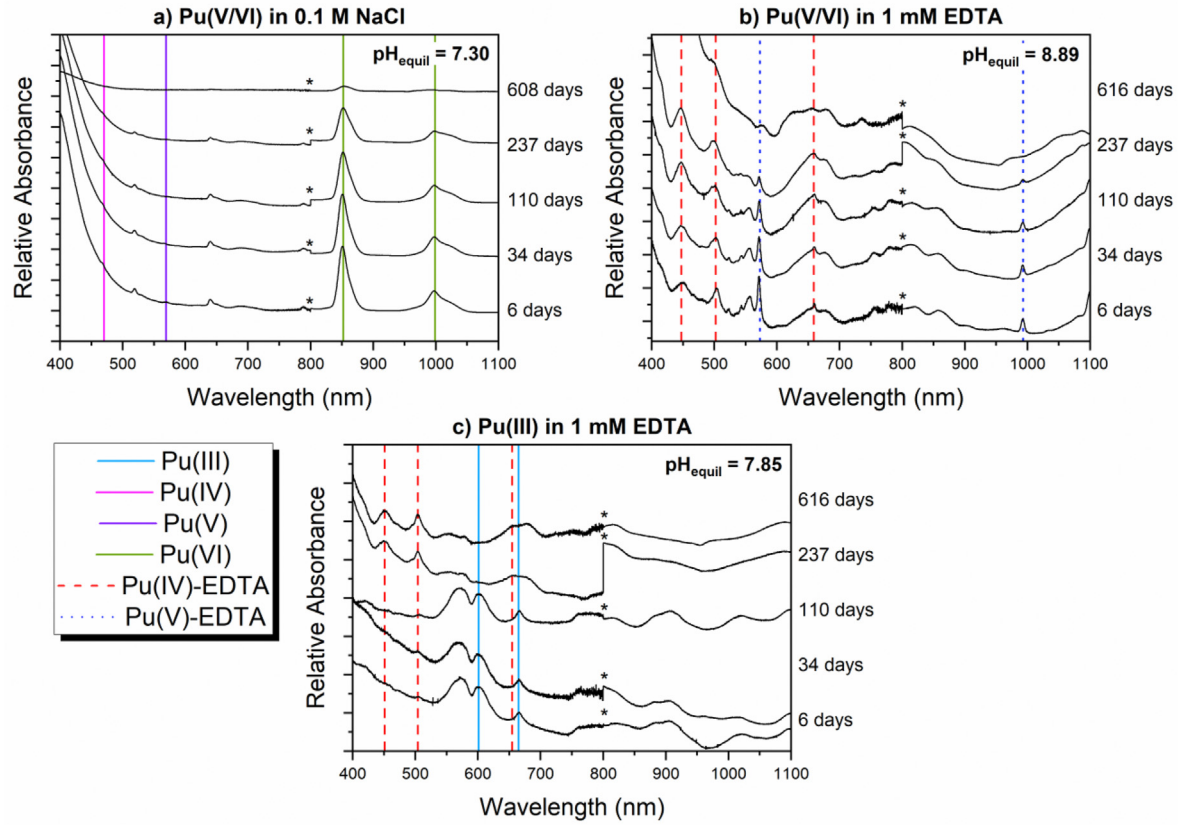


Fig. 3. Time-resolved UV–Vis–NIR absorption spectra of experiments initially adjusted to pH 8: (a) Pu(V/VI) in 0.1 M NaCl, (b) Pu(V/VI) in 1 mM EDTA, and (c) Pu(III) in 1 mM EDTA. Solid lines signify plutonium aquo ion peaks (Pu(III) = blue, Pu(IV) = magenta, Pu(V) = purple, and Pu(VI) = green). Red dashed lines signify Pu(IV)-EDTA peaks and blue dotted lines signify Pu(V)-EDTA ion peaks. Stars represent an instrumental artifact caused by a detector/grating change. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

those of AlMahamid et al. (1996), who reported complete oxidation of Pu(III) to Pu(IV)-EDTA within 19 min under conditions similar to this study ([Pu] = 10^{-3} M, L/M ≈ 6, pH ≈ 6). While a much slower, but nonlinear, change in oxidation state occurs in our study, we are confident these results are real and do not result from oxygen contamination into the system, as oxygen monitoring, experimental storage, and sampling were conducted under very controlled conditions. Instead, we hypothesize that the discrepancy between our and previously reported oxidation rates is due to significant differences in the level of oxygen control combined with radiolysis effects. It is likely that residual trace oxygen was present in previous experiments (e.g., due to older glovebox technology). Additionally, AlMahamid et al. (1996) utilized ^{239}Pu whereas we used ^{242}Pu. ^{239}Pu should exhibit faster oxidation than the current work due to the alpha radiolysis of water, which can produce oxidizing byproducts.

Although using ^{242}Pu reduced radiolysis effects in our system, they were not completely eliminated. Due to a lack of oxidative properties, we do not believe EDTA was the oxidizing agent in the Pu(III)-EDTA system. Instead, we propose that oxidizing radiolysis byproducts slowly accumulated leading to accelerated rates of oxidation with time that resulted in complete oxidation of Pu(III) to form a stabilized Pu(IV)-EDTA complex. Unlike the Pu(V/VI)-EDTA system, a rough calculation suggests that enough H_2O_2 and oxidizing free radicals were produced in-situ through the alpha radiolysis of water between 110 and 237 days to facilitate oxidation of Pu(III)-EDTA to Pu(IV)-EDTA (see Appendix). Pu(V/VI)-EDTA experiments at pH 8 stabilized a mixture of Pu(IV)- and Pu(V)-EDTA complexes after 616 days, whereas Pu(III)-EDTA experiments at the same pH only oxidized to Pu(IV)-EDTA. While radiolysis products are capable of oxidizing plutonium to Pu(V) and Pu(VI) (Büppelmann et al., 1986), we hypothesize the oxidation stopped at Pu(IV)-EDTA due to the overwhelming thermodynamic stability of Pu(IV)-EDTA complex(es) as compared to Pu(V)-EDTA complexes. Ultimately, it is both radiolytic oxidation combined with the preferential stabilization of the Pu(IV)-EDTA complex that explains the long-term outcome observed in the Pu(III)-EDTA system.

3.2.4. Comparison to available thermodynamic data

Aqueous plutonium concentrations ($[Pu]_{aq}$) and experimental pe-pH measurements (t = 54, 110 days) were compared with thermodynamic models for Pu(III)- and Pu(IV)-EDTA (Fig. 5) based on equilibrium constants from Hummel et al. (2005), Grenthe et al. (2020), and Rai et al. (2008). Example calculations and discussion of model selections are provided in the Appendix.

Experimental pe-pH measurements at t ≤ 110 days for Pu(III)-EDTA lie within the Pu(III) stability region of the diagram (Fig. 5a). This agrees with our Pu(III)-EDTA spectrophotometry data, where oxidation to Pu(IV)-EDTA was not observed until t > 110 days. E_h measurements at t > 110 days were not possible due to limited solution volume, so we cannot determine if an increase in pe accompanied the oxidation of Pu(III)-EDTA to Pu(IV)-EDTA.

$[Pu]_{aq}$ measurements for Pu(III)-EDTA were accurately described by the chosen solubility models (Hummel et al., 2005; Tasi et al., 2018). At pH < 6, $[Pu]_{aq}$ values were equivalent to initial plutonium concentrations and below $Pu(OH)_3$(am) solubility limits (Fig. 5b), whereas at pH > 6, $[Pu]_{aq}$ values were underpredicted by the $Pu(OH)_3$(am) solubility model but accurately described by the

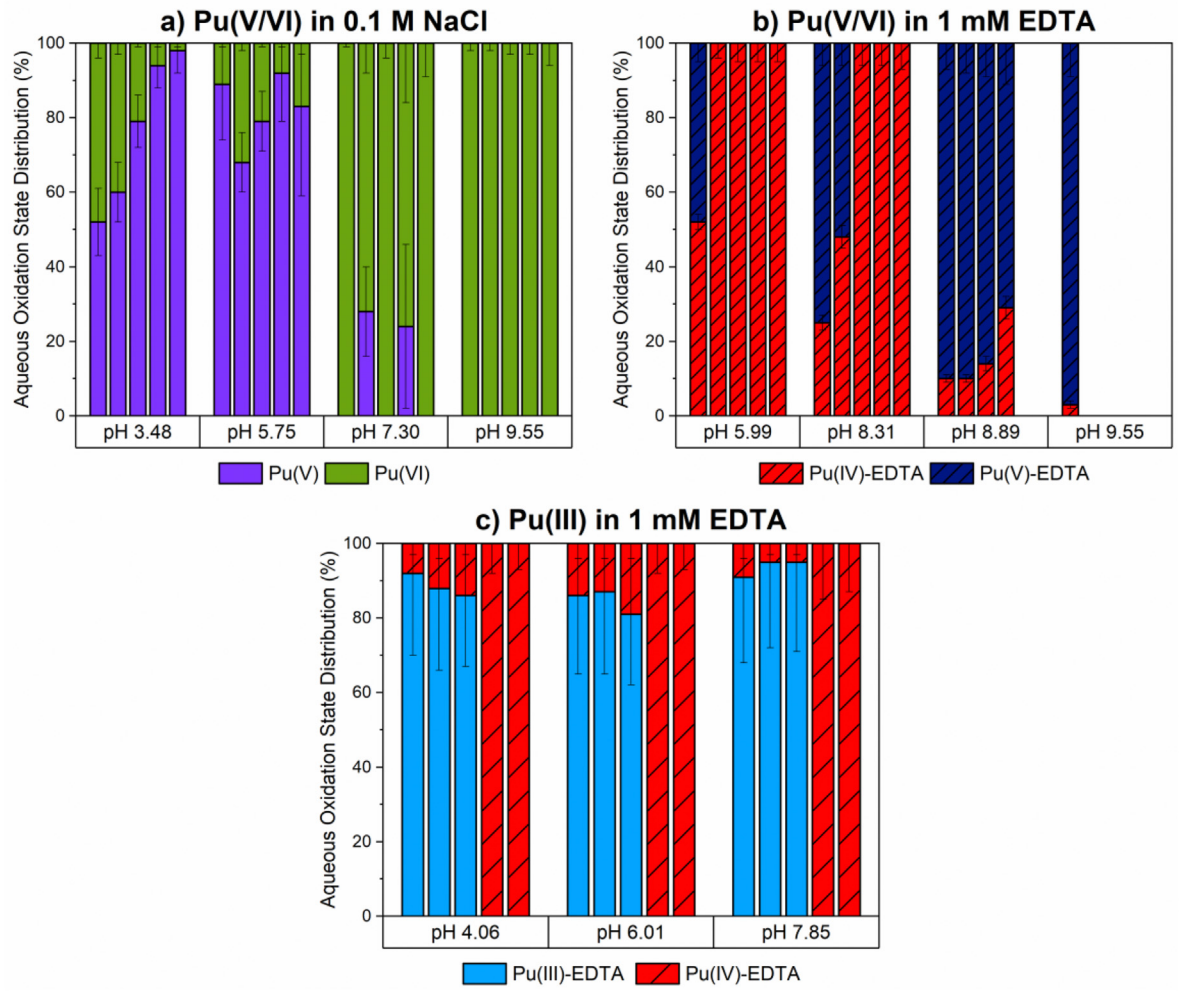


Fig. 4. Plutonium oxidation state distribution of (a) Pu(V/VI) in 0.1 M NaCl, (b) Pu(V/VI) in 1 mM EDTA, and (c) Pu(III) in 1 mM EDTA as a function of equilibrium pH and time. Time increases from left to right at each pH (t = 6, 34, 110, 237, and 616 days).

Pu(III)-EDTA model. This indicates that the formation of Pu(III)-EDTA complexes increased the solubility of Pu(III) under these conditions. We observed limited spectroscopic changes upon Pu(III)-EDTA complexation, so this model comparison provides further evidence that Pu(III)-EDTA complexes formed and were stabilized in solution before oxidation to Pu(IV)-EDTA was observed.

Pu(V/VI)-EDTA pe-pH measurements lie within the predominance region of aqueous Pu(IV)-EDTA, and the Pourbaix diagram predicted precipitation above pH 5 (Fig. 5a). While Pu(V/VI)-EDTA experiments approached Pu(IV)-EDTA stabilization, those at pH > 8 were predominantly Pu(V)-EDTA at 110 days and precipitation did not occur until pH > 9. A dashed line representing the pe-pH measurements of the Pu(V/VI) experiments without EDTA is also presented in Fig. 5a. Comparing this line to the Pu(V/VI)-EDTA data makes it clear that the addition of EDTA lowered the pe of the system (i.e., provided a more reducing environment). This supports our hypothesis that EDTA is the source of plutonium reduction in the Pu(V/VI)-EDTA system.

PuO_2(am,hyd) and Pu(IV)-EDTA solubility models underpredicted $[Pu]_{aq}$ measurements for Pu(V/VI)-EDTA experiments (Fig. 5c). At pH > 8, multiple plutonium oxidation states are present in solution (Fig. 4b). However, at pH < 8, Pu(V/VI)-EDTA spectroscopic results for 237–616 days showed only Pu(IV)-EDTA in solution, which should be represented by the models.

The inconsistency between experimental observations and model predictions suggests incomplete thermodynamic models. Such inconsistencies could stem from disagreements on the speciation of Pu(IV)-EDTA. However, other possible explanations include: (i) Pu(III/V/VI) are present at concentrations below detection limits for UV–Vis–NIR but contribute to the total plutonium concentration measured by ICP-MS; and (ii) reduction and Pu(IV)-EDTA precipitation kinetics are slower than the 616-day time-frame of the study (i.e., precipitation reactions may occur over elongated time periods thus we did not reach steady state). Any oxidation state changes large enough to impact solubility measurements should be visible in the spectrophotometric data, suggesting that (i) is not a strong argument. However, it is possible that (ii) impacts our system since we observed continued changes in Pu(V/VI)-EDTA spectra at the longest time points. Ultimately, elevated concentrations observed in both the Pu(III)- and Pu(V/VI)-EDTA systems with respect to plutonium solid phases reflect the favored stability of aqueous Pu-EDTA complexes and suppression of thermodynamically-stable precipitate formation under the circumneutral and slightly alkaline conditions expected in environmental systems.

4. Conclusions

Our results showed the predominance of Pu(IV)-EDTA

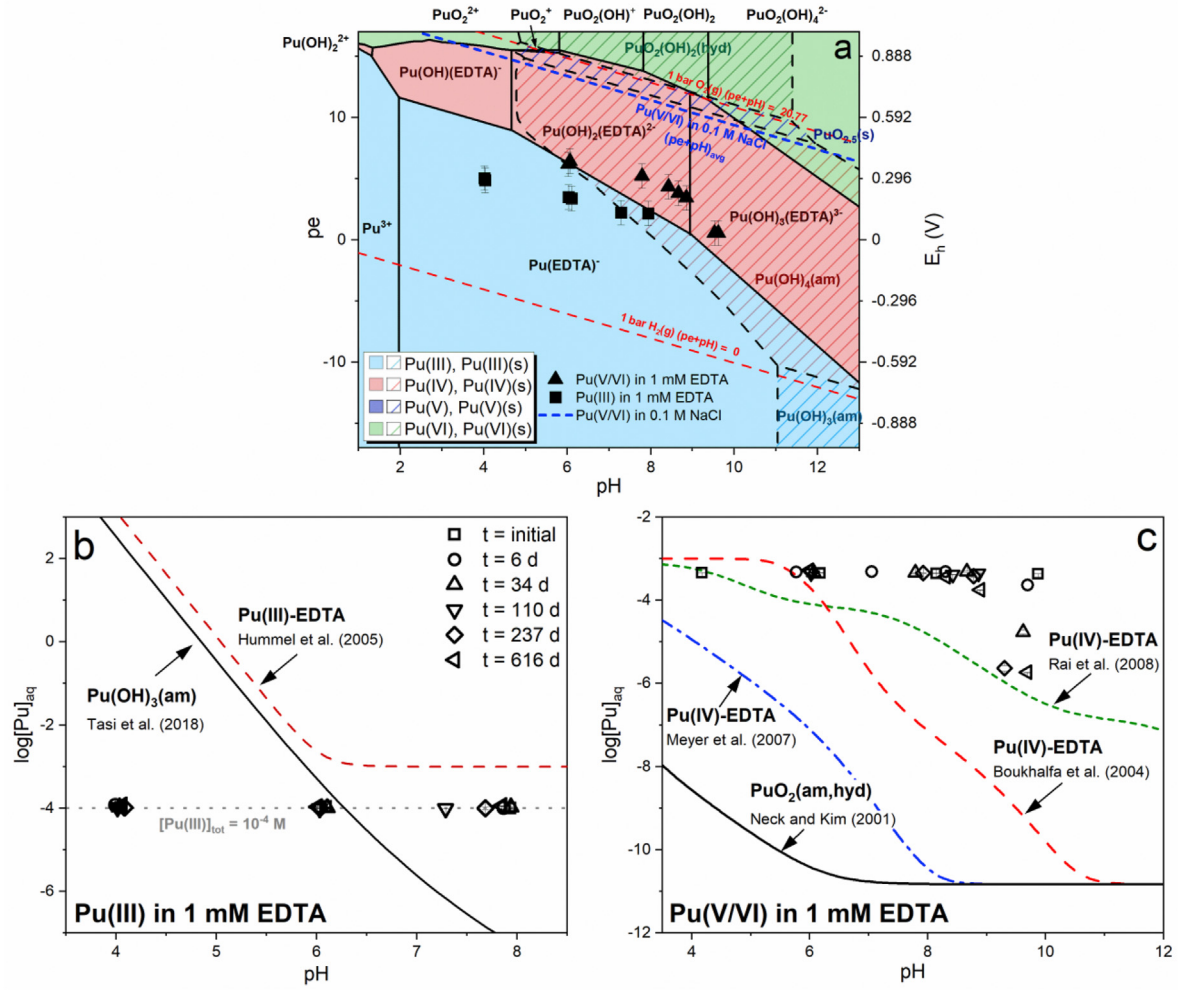


Fig. 5. (a) Pourbaix (pe-pH) diagram of the Pu-EDTA system calculated for $[Pu]_T = 10^{-4}$ M, [EDTA] = 1 mM, and $I = 0.1$ M using equilibrium constants from the literature (Grenthe et al., 2020; Guillaumont et al., 2003; Hummel et al., 2005; Rai et al., 2008). Experimental pe-pH measurements at t ≤ 110 days for Pu(V/VI)-EDTA and Pu(III)-EDTA systems are represented by solid triangles and solid squares, respectively. Solid and dashed black lines correspond to redox borderlines between aqueous and solid plutonium species, respectively, red dashed lines show the stability field of water, and the blue dashed line represents pe-pH measurements of Pu(V/VI) experiments conducted in 0.1 M NaCl. The log $[Pu]_{aq}$-pH diagrams from ICP-MS measurements are shown for (b) Pu(III) in 1 mM EDTA and (c) Pu(V/VI) in 1 mM EDTA at t = 6–616 days. Thermodynamic models for $Pu(OH)_3$(am) and PuO_2(am,hyd) solubility are represented by black solid lines (Neck and Kim, 2001; Tasi et al., 2018), and Pu(III)-EDTA and Pu(IV)-EDTA solubility models are represented by dashed lines (Boukhalfa et al., 2004; Hummel et al., 2005; Meyer et al., 2007; Rai et al., 2008). All solubility models were calculated with [EDTA] = 1 mM and ionic strength corrected to $I = 0.1$ M NaCl using the SIT model (Ciavatta, 1980; Pitzer, 1991). Error bars represent uncertainty propagated from E_h and ICP-MS measurements. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

complexes compared to Pu(III)-, Pu(V)-, and Pu(VI)-EDTA complexes when plutonium was in the presence of EDTA for long time periods (t ≤ 616 days) under circumneutral and alkaline conditions. Spectrophotometric studies of Pu-EDTA as a function of ligand-to-metal ratio (L/M) and pH allowed us to identify and quantify four distinct Pu(V)-EDTA absorption bands and to determine the effect of EDTA on Pu(III) spectrophotometry. We concluded that only 1:1 Pu(V)-EDTA complex(es) form and calculated $\log K(Pu^{V}O_2(EDTA)^{3-}) = 3.6 \pm 0.3$. Time-resolved spectrophotometry of Pu(III) and Pu(V/VI) in EDTA showed oxidation or reduction, respectively, of plutonium and the formation of stable Pu(IV)-EDTA complex(es). EDTA greatly accelerated the rate of Pu(V/VI) reduction, and the proposed reduction mechanism involves amine lone-pair electron donation and the oxidative decarboxylation of EDTA. Although Pu(V/VI) experiments trended towards Pu(IV)-EDTA stabilization, we observed that Pu(V)-EDTA complex(es) can persist up to 616 days under environmentally-relevant, alkaline conditions. Oxidation of Pu(III)-EDTA to Pu(IV)-EDTA occurred after 110 days, instead of within 15 minutes as reported in previous literature. We suggested that this difference stems from the likely presence of residual oxygen in previous experiments and the use of different plutonium isotopes, resulting in a slower buildup of byproducts from the alpha radiolysis of water. Finally, we showed that current speciation models do not accurately describe our experimental observations. A comprehensive understanding of plutonium complexation and associated redox effects is of the utmost importance for final disposal of transuranic waste in deep geologic repositories, yet the discrepancies identified in our work suggest that further research into Pu-EDTA solubility and mobility under environmentally-relevant conditions is needed. Ultimately, these findings provide insights into EDTA- and radiolysis-driven redox interactions of plutonium, which contribute to the understanding required for predicting the fate and transport of plutonium in repository and near-surface environmental settings.

Credit author statement

Nicole A. DiBlasi: Conceptualization, Methodology, Formal

analysis, Investigation, Visualization, Writing – original draft, Writing – review & editing, Ezgi Yalçintas: Methodology, Investigation, Floyd E. Stanley: Investigation, Formal analysis, Writing – review & editing, Donald T. Reed: Conceptualization, Validation, Resources, Supervision, Funding acquisition, Writing – review & editing, Amy E. Hixon: Conceptualization, Resources, Supervision, Funding acquisition, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2021.129741.

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