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Plutonium (VI) reduction to (V) by hydroxamate compounds at environmentally relevant pH

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Abstract

Natural organic matter is known to influence the mobility of plutonium (Pu) in the environment via complexation and reduction mechanisms. Hydroxamate siderophores have been specifically implicated due to their strong association with Pu. Hydroxamate siderophores can also break down into di and mono-hydroxamates and may influence Pu oxidation state, and thereby its mobility. In this study we explored the reactions of Pu(VI) and Pu(V) with a mono-hydroxamate compound (acetohydroxamic acid, AHA) and a tri-hydroxamate siderophore desferrioxamine B (DFOB) at environmentally relevant pH (5.5-8.2). Pu(VI) was instantaneously reduced to Pu(V) upon reaction with AHA. The presence of hydroxylamine was not observed at these pHs; however, AHA was consumed during the reaction. This suggests that the reduction of Pu(VI) to Pu(V) by AHA is facilitated by direct one electron transfer. Importantly, further reduction to Pu(IV) or Pu(III) was not observed, even with excess AHA. We believe that further reduction of Pu(V) did not occur because Pu(V) does not form a strong complex with hydroxamate compounds at circum-neutral pH. Experiments performed using desferrioxamine B (DFOB) yielded similar results. Broadly, this suggests that Pu(V) reduction to Pu(IV) in the presence of natural organic matter is not facilitated by hydroxamate functional groups and that other natural organic matter moieties likely play a more prominent role.

Introduction

Plutonium (Pu) represents a major environmental and public health hazard due to its long half-life (^{239}Pu, $t_{1/2}$ ~24000 yrs.), toxicity and ability to migrate (kilometers) in the environment [1, 2]. Understanding the fate of actinides in the environment requires knowledge of the fundamental biogeochemical processes that control actinide speciation, precipitation and transport. One such example is the ability of microorganisms to react with Pu through surface adsorption, or the secretion of chelating agents (e.g., siderophores). Siderophores are produced by microorganisms and plants to chelate insoluble Fe(III), making it available for cellular uptake [3]. Hydroxamate siderophores (e.g., DFOB) range in concentration from 0.1 to 0.01 μM in soils [4, 5] and may also influence Pu transport in the environment through complexation and redox reactions [6-9]. The hydroxamate groups found in many siderophores are O,O ligands that form strong complexes with acidic metal cations, including many actinides (Fe(III), Pu(IV), Np(IV)) [10-15]. The degradation of siderophores in the environment leads to the release of simple mono and di-hydroxamates with lower metal affinities [16, 17] (Figure 1a).

Acetohydroxamic acid (AHA) is a mono-hydroxamic acid found in the environment and has been used in nuclear fuel processing to separate Np and Pu from U [18, 19]. The majority of reactions involving actinides and AHA have been studied in advanced PUREX separation processes, which utilize high concentrations of nitric acid (1-4 M) with actinides at mM concentrations [12, 19, 20]. In acidic solutions AHA undergoes hydrolysis reactions (Figure 1b), leading to the formation of hydroxylamine and the reduction of Pu(IV) to Pu(III). These studies reveal that reduction of Pu(VI) and Np(VI) occurs by a rapid electron exchange with AHA (Figure 1c) followed by slow continued reduction from acid hydrolysis products (hydroxylamine) [12, 20, 21]. The formation of an AHA-metal ligand has variable effects on hydrolysis rates with Fe(III)-AHA ligands increasing hydrolysis rates while Np(IV)-AHA decreases the rate [10, 11, 22, 23]. The reactions of Pu-AHA ligands at environmentally relevant pH (5-8) have not yet been investigated and may play a role in the fate of actinides complexed by siderophore breakdown products (mono and di-hydroxamates) at contamination sites.

In this study, we explored the stability of Pu-hydroxamate compounds under environmentally relevant solution conditions. The measurement of Pu redox states and AHA hydrolysis products (hydroxylamine) allowed us to determine if hydrolysis of AHA is controlling Pu reduction. Reactions of Pu(VI) and Pu(V) with DFOB were also explored to determine if chelation by hydroxamate siderophores influences reduction mechanisms. The results are used to identify the role that hydroxamate compounds are likely to play in Pu complexation and redox transformations under environmentally relevant conditions.

MATERIALS AND METHODS

Plutonium Stock Solutions. A Pu stock consisting of 99.8% ^{242}Pu, 0.40% ^{241}Pu, 0.11% ^{240}Pu, 0.005% ^{239}Pu, and 0.0046% ^{238}Pu, by atomic percent, was used in all experiments. Three Pu stocks were prepared: Pu(IV), Pu(VI) and Pu(V). The Pu(IV) stock was generated during the column purification and the Pu(VI) and Pu(V) stocks were used for the AHA and DFOB reduction studies. The Pu stock was first purified using a Bio Rad AG 1–8X (100-200 mesh) resin column [24]. The Pu was converted to Pu(IV) using saturated $NaNO_2$ in 8 M nitric acid, heated to 50°C and cooled to room temperature. The Pu(IV) was then loaded on a resin column and rinsed with 8 M nitric acid followed by 9 M HCl. Pu(III) was eluted from the column using hydroiodic acid (HI) in 9 M HCl (1:25 ratio). The purified Pu stock was evaporated to near dryness and re-dissolved in concentrated nitric acid 5 times to remove excess HI. After removal of excess HI the stock was re-dissolved in 0.1 M nitric acid producing a 4.27 mM Pu(IV) stock (Figure S1a). Pu(VI) stocks were prepared using electrochemistry[6, 25]. The purified Pu(IV) stock was added to an electrochemical cell and 0.1 M $NaNO_3$ was used as the electrode solution. The stock was oxidized at 1.95 V for 5 days. The oxidation state of the stock was verified using Uv-Vis-NIR spectroscopy and was > 99% Pu(VI) (Figure S1b). A Pu(V) stock was prepared by pH adjusting a portion of the Pu(VI) stock to pH 3 using 1 M NaOH. The pH adjusted Pu(VI) stock was then reacted with 50 mM hydrogen peroxide (H_2O_2) and heated to 50°C for 1 hour to produce Pu(V) and decompose the remaining H_2O_2 to water[6]. The purity of the Pu(V) stock was > 99% when measured with UV-Vis-NIR (Figure S1c).

Plutonium Hydroxamate Reaction Conditions. Solutions of Pu(VI) (100 µM) were pH adjusted to 5.7-6.0 using 1M sodium hydroxide (NaOH) or sodium bicarbonate ($NaHCO_3$) prior to the addition of AHA (acetohydroxamic acid 98%, sigma-aldrich) or DFOB (deferoxamine mesylate salt ≥92.5%, sigma-aldrich) . The pH adjusted Pu(VI) was reacted with 25, 50, 100, 200 and 1000 µM AHA. Samples were immediately measured using Uv-Vis-NIR spectroscopy to monitor changes in Pu oxidation state. Spectra were collected using an Agilent 6000i UV-Vis-NIR spectrometer scanning from 400-900 nm with a 0.5 nm step size and 0.2 sec integration time. Multiple Pu(VI) complexes with OH and CO_3^{2-} were observed after pH adjustment, making it difficult to quantify changes in Pu oxidation state. A portion of the sample was acidified (0.1 M HCl) to quantify the percentage of Pu(VI) and Pu(V). A separate set of Pu-AHA experiments were also conducted, starting with Pu(V) (100 µM, pH adjusted to 5.6 with NaOH) reacted with 200 µM AHA. The reaction of Pu(VI) with DFOB was measured using UV-Vis-NIR spectroscopy with 100 µM Pu(VI) pH adjusted to 5.5 using 1 M NaOH and 200µM DFOB (Deferoxamine mesylate salt ≥92.5%, sigma-aldrich). A Pu(IV)-DFOB spectrum was also measured by adding 100 µM Pu(IV) directly to a 200 µM DFOB solution, resulting in a pH of 2.5 which was immediately adjusted to pH 5.5 using 1 M NaOH. All experiments were conducted under ambient laboratory lighting conditions. However, samples were wrapped in aluminum foil (to limit possible light-induced redox processes) and placed on a rotary shaker at 150 rpm during the 7 day reaction.

GC-MS of Plutonium Hydroxamate Reactions. Concentrations of AHA and hydroxylamine were monitored using gas chromatography-mass spectrometry (GC-MS) using a method modified from Vincenti et al., 1995 [26]. Aqueous solutions (300uL) of Pu reacted with AHA were derivatized in 1.5 mL amber glass vials with polytetrafluoroethylene (PTFE) lined caps with 15 uL of n-hexyl chloroformate and 30 uL pyridine for five minutes in an ultrasonic bath. After derivatization, 300 uL of n-hexane was added and samples were re-capped and sonicated for another five minutes. The vials were then vortexed and the hexane layer was transferred into a vial for GC-MS analysis.

The hexane extracts were analyzed on an Agilent 6890 GC equipped with a 5973 MS detector and a 30 m length 5% diphenyl dimethyl siloxane HP5-MS capillary column, with a 0.25 mm internal diameter and 0.25 µm film thicknesses. A 1 µL volume of sample was injected into the splitless inlet at 280°C using He as the carrier gas at 44.1 mL/minute for 30 seconds. The flow rate into the column was maintained at 1 mL/minute. The oven temperature was held at 50°C for three minutes, followed by heating 20°C/min to 300°C and held at 300°C for 10 minutes. A selective ion monitoring (SIM) method was developed to lower the background signal from the n-hexyl chloroformate and increase detection limits. Ions fragments characteristic of AHA and hydroxylamine were determined by scanning the mass range from 50-200 m/z (Figure S2). Concentrations of AHA were measured from ion fragments at 76.1 and 120.1 m/z, with hydroxylamine measured at 78.1 and 122.2 m/z (Figure S2). Each ion was scanned using a 60 ms dwell time. Ions for AHA were measured from 10 to 15 minutes while hydroxylamine was measured from 15 to 20 minutes. Calibration curves from 1000 µM to 0.5 µM were generated for AHA and hydroxylamine.

RESULTS AND DISCUSSION

Plutonium Acetohydroxamic Acid Redox Reactions. We monitored the redox state of 100 µM Pu(VI) reacted with 25, 50, 100, 200 and1000 µM AHA using UV-Vis-NIR spectroscopy. While these concentrations do not represent those seen in nature, they allowed us to measure the reduction of Pu by hydroxamates without the use of LaF_3 co-precipitation in strong acids[27] that would rapidly hydrolyze hydroxamate compounds, confounding the interpretation of Pu redox. In the environment, soluble Pu(VI) is predominately complexed by OH^- and CO_3^{2-} [28, 29]. The redox potential of the Pu(VI) to Pu(IV) transition changes due to OH^- and CO_3^{2-} complexation, with a more reducing environment required to reduce $Pu(VI)CO_3$ complexes [30]. To evaluate possible ligand effects on redox transformations, we performed our experiments using both OH^- and HCO_3^- buffers. The pH of the Pu(VI) solutions was adjusted with NaOH (pH 5.7) or $NaHCO_3$ (pH 6.0) and spectra were collected immediately after the addition of AHA, with additional spectra collected over seven days.

The reaction of Pu(VI) with AHA at pH 5.7 (NaOH) resulted in the immediate formation of a Pu(V) peak at 570 nm at all AHA concentrations investigated (Figure 2a). After 7 days, the pH decreased from 5.7 to 5.2, likely due to the generation of acetic acid during AHA oxidation. The Pu(VI) peak at 831 nm is not present at concentrations of AHA ≥ 50 µM and a stable Pu(V) peak is present during the course of the 7 day reaction. Auto-reduction of the Pu(VI) control was observed, and a visible Pu(V) peak was present after 7 days. The formation of spectral features associated with Pu(IV) (Pu(IV) 470 nm and Pu(IV) colloids 620nm) was not observed, even in the presence of excess AHA (1000 µM). Even in the 25 µM AHA experiments, the Pu(VI) peak decreases in intensity immediately after the addition of AHA. These results indicate that the reduction of Pu(VI) to Pu(V) is instantaneous in the presence of AHA but that further reduction does not occur over the 7 day experiment. The Pu(V) control spectra showed a broad increase in intensity at wavelengths < 700 nm after 7 days.

A separate set of experiments using $NaHCO_3$ as a pH buffer were also performed. The Pu(VI) solutions (100 µM) were adjusted to pH 6.0 reaching a concentration of 33 mM $NaHCO_3$. The Pu(VI) peak shifted from 831 nm to 841 nm due to carbonate complexation [31, 32]. The intensity of the Pu(VI) peak decreased proportionally as the AHA concentration increased from a starting concentration of 25 µM (Figure 3a). Similar to the previous experiment, the Pu(VI) peak was not present at AHA concentrations ≥ 100 µM; yet, we again see the immediate formation of Pu(V). The pH of the $NaHCO_3$ buffered solutions shifted to 8.2 during the reaction. This resulted in further shifting of the Pu(VI) control peak to 850 nm due to carbonate complexation and broadening of the Pu(V) peak (Figure 3b). In both the NaOH and $NaHCO_3$ solutions AHA works to rapidly reduce Pu(VI) to Pu(V). This indicates that AHA is directly reducing Pu(VI) at a rate that is faster than auto-reduction mechanisms.

Quantification of Pu(VI) and Pu(V)

Given that complexation of Pu with OH or bicarbonate prevented direct quantification with Uv-Vis-NIR spectroscopy, aliquots of reactions were taken periodically and acidified with HCl (to a final concentration of 0.1 M) prior to measurement (Figure S3). Percentages were quantified by comparing baseline corrected Pu(VI) and Pu(V) peak intensity (831 and 570 nm, respectively) to unreacted Pu stock solutions in 0.1M HCl. After 24 hours, samples that were pH adjusted with NaOH, showed auto-reduction, with 14.2% of the Pu(VI) control reducing to Pu(V) (Figure 4). However, the reaction of Pu(VI) with AHA resulted in formation of 80-100% Pu(V) after one day. At the end of the 7 day reaction the Pu(VI) control had auto-reduced further, resulting in 55% Pu(V). The samples reacted with AHA maintained Pu(V) concentrations of 96-100% after 7 days. The acidified spectra showed no signs of Pu(IV) after 7 days. The Pu(VI) control in the bicarbonate buffered experiment formed 16.6 % Pu(V) due to auto-reduction after 7 days. Concentrations of AHA ≥ 100 μM resulted in the formation of 74-89% Pu(V). The amount of Pu(VI) formed in the bicarbonate buffered experiments was lower (89%) when compared with the NaOH buffered system that achieved 100% reduction of Pu(VI) (Figure 4). The reduction of Pu(VI) by AHA exceeded auto-reduction mechanisms in both the NaOH and $NaHCO_3$ buffered experiments. Overall, lower concentrations of Pu(V) were observed in the $NaHCO_3$ buffered experiments. This may be the result of the elevated pH (8.2) and stabilization of Pu(VI) by carbonate complexation. The standard reduction potential (E°) for the Pu(VI) to Pu(IV) transition shifts when Pu(VI) is complexed by OH^- or CO_3^{2-}. Complexation by OH^- results in E° values of 1.32 - 1.39 V while CO_3^{2-} complexes have lower redox potentials (0.609 - 0.762 V) [30]. This indicates that Pu(VI)OH complexes are reduced before CO_3^{2-} complexes and supports the differences we observed in Pu(VI) reduction by AHA (Figure 4).

Quantification of AHA Reaction Products

Concentrations of AHA and hydroxylamine were measured by GC-MS over a 7 day period to determine if AHA is consumed during the reaction, with hydroxylamine participating in the reduction. Chromatograms of Pu(VI) reacted with AHA showed no traces of hydroxylamine throughout the reaction (Figure 5). Pu(VI) samples reacted with 25 and 50 μM AHA showed no measurable AHA after 24 hours of reaction with 100μM Pu(VI) in both buffers (Figure 6). At AHA concentrations ≥ 100 μM an average of 80 μM (± 18 μM) was consumed during the reaction. The consumption of AHA occurs quickly, within the first hour of the reaction and AHA concentrations remain constant in the presence of Pu(V) (Figure. 6).

These results support conclusions from the UV-Vis-NIR spectra which show a rapid reduction of Pu(VI) to Pu(V), with no further reduction of Pu(V) in the presence of excess AHA. The concentrations of AHA consumed in the reaction do not appear to have a direct stoichiometric relationship with the amount of Pu(VI) reduced, as we would expect 100 μM AHA to be consumed as 100 μM Pu(VI) is reduced by a one electron transfer. This offset is potentially caused by reaction intermediates produced as AHA is oxidized, with concomitant auto reduction mechanisms and Pu-AHA complex formation, as further discussed below [19, 33].

A separate set of experiments starting with 100 μM Pu(V) and 200 μM AHA was also performed (Figure 7). The UV-Vis-NIR spectra remain constant over 7 days and show no signs of Pu(IV) formation. At pH 5.7 Pu(IV) is insoluble and would form Pu-oxide colloids. If this were to occur we would expect to see a decrease in the Pu(V) peak intensity and a Pu(IV) colloid absorption band around 510 and 620 nm [34, 35]. These results indicate that at circum-neutral pH, AHA reduces Pu(VI) to Pu(V) but does not further reduce Pu(IV) (Figure 7.). Previous studies of Pu(VI) AHA reactions in 1-4 M nitric acid have observed an instantaneous reduction of Pu(VI) to Pu(V) proceeded by a slow reduction to Pu(IV) and Pu(III) over 24 hours [18]. Under acidic conditions, the rapid reduction of Pu(VI) by AHA was attributed to a direct electron exchange between Pu(VI) and AHA followed by the rate limited reduction of Pu(V) to Pu(IV) by hydroxylamine due to acid hydrolysis of AHA [18, 20, 36]. At the higher, environmentally relevant pHs explored in this paper, Pu(VI) reduction to Pu(V) still proceeds. However, further reduction is limited by the fact that acid hydrolysis of AHA does not occur at these pHs.

Pu(VI) DFOB Reactions

The experiments described above indicate that the reaction of Pu(VI) with the mono-hydroxamic acid AHA results in the formation of Pu(V). However, it is possible that chelating hydroxamate siderophores have a greater affinity for Pu and could drive further reduction. To test this, we explored the reactions of Pu(VI) with DFOB. The siderophore DFOB contains three hydroxamate functional groups that may result in the reduction of Pu(VI) to Pu(IV) via a two electron exchange, bypassing the formation of Pu(V). One earlier study of Pu-DFOB interactions suggested that a Pu(IV)-DFOB complex can be produced when starting from Pu(III), Pu(V), or Pu(VI)[37]. The oxidation of Pu(III) to Pu(IV) and reduction of Pu(VI) to Pu(V) was said to be rapid while the reduction of Pu(V) to Pu(IV) was said to be pH dependent (with the rate increasing with pH). However, no detail was provided as this study has only been reported as a conference proceeding.

Solutions of Pu(VI) (100 µM) were pH adjusted to 5.5 with 1M NaOH, reacted with 200 µM DFOB and measured using UV-Vis-NIR spectroscopy (Figure 8). These experiments show that Pu(VI) is reduced to Pu(V) instantaneously upon reaction with DFOB, with no Pu(IV)-DFOB complex observed over 7 days (Figure 8). The results suggest that Pu(VI) is capable of forming a complex with DFOB that facilitates an electron exchange, forming Pu(V). The complexation of Pu(V) by DFOB and further electron exchange to form Pu(IV) is not apparent.

In the environment natural organic matter (NOM) and micro-organisms influence the mobilization of radionuclides through complexation, chelation, sorption and redox reactions [6, 7, 9, 38]. However, a mechanistic understanding of redox reactions with NOM and radionuclides remains enigmatic. Evidence suggests that Pu in the environment is strongly associated with hydroxamate siderophores [8, 9, 39]. Hydroxamate siderophores (DFOB) form O,O complexes with metals that are dependent on the charge and radius of the cation in solution [40]. These properties are related to the affinity of a metal for OH^- resulting in hydrolysis reactions in aqueous solutions [41]. For example, tri and tetra-valent cations (Fe(III), Al(III) and Pu(IV)) have a strong affinity for OH^- and generate acid in solution via hydrolysis, while di-valent cations (Ca(II) , Mg(II)) have a low affinity for OH^- and negligible hydrolysis reactions [41, 42]. The stability constants of metals and OH^- (logK (OH^-)) in solution have been used as a proxy for predicting the affinity of metal ions to O,O donor ligands [43, 44] (Figure 9a). The behavior of Fe-hydroxamate ligands can provide some context into the reactions of Pu with hydroxamates.

Ferric iron is strongly bound by DFOB and AHA with $\log\beta_1$ values of 30.9 and 11.4 respectively[17, 40, 45]. When Fe(III) chelated by DFOB enters the cell it is reduced to Fe(II), which has a lower binding affinity for the siderophore ($\log\beta_1$ 10.0) [45]. This results in the release of Fe from the siderophore for cellular processes. DFOB has three hydroxamate functional groups and shows stronger stability complexes for Fe(III) and Pu(IV) when compared to the mono-hydroxamate AHA (Figure 9b). However, divalent cations show lower stability constants, with similar values for both DFOB and AHA (Figure 9a). The binding of Fe and Pu to O,O donor ligands are therefore correlated to the affinity for OH^- ions in solution (logK OH^-) and the charge of the metal cation (Figure 9). The stability constants for Pu(III) and Pu(IV) with AHA and DFOB have been measured in previous studies [5, 14] however, the stability constants for Pu(VI) and Pu(V) have not been reported in the literature. The logK(OH^-) values for Pu(VI) and Pu(V) are 8.5 and 1.2 - 4.2 respectively [46]. This indicates that Pu(VI) behaves more like a trivalent acidic cation in solution while Pu(V) behaves as a divalent with lower affinity for O,O ligands (Figure 9b). The formal charge assigned to PuO_2^{2+} and PuO_2^+ species (2+ and 1+ respectively) do not represent the actual charge in solution for each ion. The effective charges for PuO_2^{2+} and PuO_2^+ were found to be 3.3 and 2.2 respectively [47].

Our results suggest that Pu(VI) is capable of forming a complex with AHA (and DFOB) that results in the immediate exchange of an electron, forming Pu(V). However, Pu(V) is predicted to behave as a divalent cation with a lower affinity for AHA (and DFOB) that does not allow a complex to form that further reduces Pu (Figure 9). Hydrolysis of AHA and the formation of the reducing agent hydroxylamine do not appear to facilitate the reduction of Pu at environmentally relevant pHs. The hydrolysis of AHA follows pseudo-first order kinetics with the rate dependent on the concentration of H^+ [48]. As solution pH increases above 2, the hydrolysis rate decreases exponentially and AHA is predicted to be stable (Figure S4). A one electron oxidation of AHA has been shown to produce nitric oxide, nitrous acid and nitroxyl radicals [19, 33]. These reaction intermediates may play a role in the reduction of Pu(VI) in addition to auto-reduction mediated pathways.

Our research shows that Pu(VI) and (V) are not reduced to Pu(IV) by hydroxamate compounds at environmentally relevant pH (5.5-8). The majority of studies on Pu(VI) and Pu(V) interactions with natural organic matter and microbes show reduction to Pu(IV) [6, 49-51]. Despite this observation, we still do not know which biomolecular functional groups facilitate reduction to Pu(IV). Recent evidence reveals that hydroxamate compounds in soils and sediments are strongly associated with Pu and may influence mobilization in the environment [8, 39]. Previous studies of Pu AHA redox reactions in 1-4 M nitric acid show reduction of Pu(VI) to Pu(III) [18-20]. In contrast, our experiments at circum-neutral pH show that hydroxamate compounds are only capable of reducing Pu(VI) to Pu(V). The weak complexation of Pu(V) with hydroxamic acid functional groups limits the possible reduction to less soluble Pu(IV). While hydroxamate-containing siderophores may play an important role in Pu(IV) complexation and mobilization, other electron-donating components of natural organic matter (e.g. quinones) likely play a more prominent role in Pu(V) reduction. This study indicates that the reduction of Pu(V) to (IV) by NOM and microbes is not facilitated by hydroxamates and highlights the need for a basic understanding of Pu organic reactions at environmentally relevant pH.

Figure Captions

Figure 1. Structures and reaction pathways of hydroxamate compounds. (a) Structures of the tri-hydroxamate siderophore DFOB and mono-hydroxamate AHA. (b) Hydrolysis reaction of AHA producing acetic acid and the reducing agent hydroxylamine. (c) Potential reaction pathways for the reduction of Pu by AHA.

Figure 2. Uv-Vis spectra of Pu(VI) (100µM) reacted with AHA (25-1000µM) pH adjusted to 5.7 using 1 M NaOH. (a) Initial spectra of Pu(VI) reacted with AHA, numbers 1-5 represent the concentration of AHA 25, 50, 100, 200, 1000 µM, respectively. Control Pu(VI) and Pu(V) solutions without AHA are shown in bold. (b-c) Peaks associated with Pu(V) (570 and 775 nm) appear upon reaction with AHA and remain throughout the 7 day reaction.

Figure 3. Uv-Vis spectra of PuO_2^{2+} (100µM) reacted with AHA (25-1000µM) pH adjusted to 6.0 using Na-Bicarbonate. (a) Initial spectra of PuO_2^{2+} reacted with AHA, numbers 1-5 represent the concentration of AHA 25, 50, 100, 200, 1000 µM respectively. The main peak associated with PuO_2^{2+} is shifted to 841 and 850 nm due to carbonate complexation. (b) Pu-AHA spectra after 24 hours showing broadening of the PuO_2^{2+} and PuO_2^{+} peaks.

Figure 4. Quantification of percent Pu(VI) and Pu(V) from UV-Vis-NIR spectra after acidification with HCl (0.1 M). (a) Pu(VI) reacted with AHA for 1 day and (b) 7 days at pH 5.7 (NaOH). (c) Pu(VI) reacted with AHA for 7 days at pH 8.2 (Na-Bicarbonate).

Figure 5. GC-MS chromatograms for AHA and hydroxyl amine. (a) Standard solutions of AHA and hydroxyl amine with retention times of 13.77 and 15.85 minutes respectively. (b) A 100 µM solution of Pu(VI) reacted with 200 µM AHA for 1 hour. A portion of the AHA still remains and no traces of hydroxyl amine were measurable.

Figure 6. Consumption of AHA during reaction with 100 µM Pu(VI) pH adjusted with NaOH or $NaHCO_3$. Decreases in AHA concentration were measured over 7 days using GC-MS. The initial concentrations of AHA used in the experiments were (a) 1000 µM, (b) 200 µM, (c) 100 µM and (d) 50 µM. The average amount of AHA consumed throughout the 7 day reaction is shown as ΔAHA. Pu(VI) reacted with 25 µM AHA showed no measurable AHA after one hour (results not shown).

Figure 7. Reaction of 100 μM Pu(V) with 200 μM AHA at pH 5.6 using 1 M NaOH to adjust the pH. (a) UV-Vis-NIR spectra of Pu(V) control and Pu(V) reacted with AHA showing no reduction to Pu(IV) over 7 days. (b) Concentrations of AHA monitored using GC-MS after 1 and 7 days determined that AHA is not being consumed while reacting with Pu(V).

Figure 8. Reaction of 100 μM PuO_2^{2+} with 200 μM DFOB at pH 5.5 using 1 M NaOH to adjust the pH. The UV-Vis-NIR spectra show an immediate reduction of Pu(VI) to Pu(V) that remains stable throughout the experiment. A reference spectra of Pu(IV) DFOB is included showing that the reaction of Pu(VI) with DFOB does not produce any spectral features associated with a Pu(IV) DFOB complex.

Figure 9. Relationship between metal hydroxide affinity (logK(OH-)) and metal O,O ligand complex formation $\log\beta_1$(ML) for DFOB and AHA. (a) Plot of metal logK(OH-) vs. $\log\beta_1$ (ML) for DFOB and AHA with linear regression fits. (b) Plot of linear fits for DFOB and AHA with data from Fe and Pu at different oxidation states. The shaded circles represent the logK(OH-) values for Pu(V) and Pu(VI) which are predicted to behave as di and trivalent cations, respectively, when reacting with AHA. Metal $\log\beta_1$(ML) and logK(OH-) values are from [2, 5, 14, 15, 17, 21-23, 40, 42, 43, 45]

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