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The Removal of Pu(IV) from Aqueous Solution Using 2,3-Dihydroxyterephthalamide-Functionalized PEI with Polymer Filtration

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ABSTRACT

Polymer filtration (PF) uses a size-exclusion ultrafiltration membrane to retain higher molecular weight species while allowing the passage of smaller species through the membrane. Metal-ion separations from aqueous streams are accomplished with PF by using water-soluble chelating-polymers (WSCP), which are appropriately sized polymers that

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have covalently attached metal-binding ligands. In this study, a new WSCP was prepared by modifying polyethylenimine (PEI) through an amide linkage to attach 2,3-dihydroxyterephthalamide (TAM) groups that have high binding constants for high valent metal cations. The TAM ligand contains a dimethylethylenediamine side chain that was found to maintain polymer solubility throughout the working pH and ionic strength ranges studied. The new WSCP (designated PDT) showed selectivity for Pu(IV) over Am(III). For example, at pH 4.5, the distribution coefficient (*D*) was 1.6×10^3 for Am(III) (14% bound) and 1.3×10^6 for Pu(IV) (99.3% bound). The Pu(IV) D increased as a function of pH, and the highest *D* was 4.8×10^6 at pH 11.4, corresponding to 99.8% bound. Varying the PDT concentration from 0.1% to 0.001% had little effect on Pu(IV) *D* values. The high formation constant of the Pu(IV)-PDT complex appears to promote the oxidation of Pu(III) to Pu(IV), even in the presence of a high concentration of reductant, 0.25-M hydroxylamine nitrate (HAN). The same high formation constant allows the TAM-containing polymer to compete with plutonium polymer formation, as plutonium absorbed on the walls of a glass vessel dissolved after contacting it with PDT for 2 days.

Key Words: Polymer filtration; Plutonium metal separations; Catecholate ligands; Ultrafiltration.

INTRODUCTION

The removal of actinides from process streams presents challenging separation problems because of the complex and unique mixture of radioactive and nonradioactive components in each stream. The classical approaches for separating actinide ions from solution include liquid–liquid extraction, ion-exchange resins, and solid-supported chelators. Although many advances have been made in the development of new extractants, ion-exchange materials, and ligands for solid supports, these techniques can have the disadvantages of slow kinetics, mixed waste formation, or colloidal interference. Few, if any, are ideal for the removal or concentration of very dilute amounts of radionuclides. Thus, new approaches to aqueous stream remediation are required that enhance kinetics of binding by elimination of two-phase reactions, eliminate organic solvents, and allow for dilute actinide-ion recovery even in the presence of colloids and high salt concentration.

Polymer filtration (PF), which uses synthetic water-soluble chelating polymers (WSCP) in combination with ultrafiltration (UF), is under development as an effective way to remove and concentrate dilute metals from aqueous streams.[1–4] Although the concept was first proposed in 1968, it is only recently that it has been implemented and applied to a number of waste remediation and processing challenges.[5–9] Polymer filtration (Fig. 1) utilizes a size-exclusion membrane to retain higher molecular weight species in the retentate while allowing the passage of smaller species through the membrane as the permeate.[10] Metal-ion separation from the stream is accomplished by chelating the metal ion with a ligand that is covalently attached to an appropriately sized water-soluble polymer. Polymer filtration has several advantages over other separation techniques: equilibrium is attained rapidly in this homogeneous system; organic solvents are avoided; no mixed-waste is produced; and soluble polymers with different ligands can be blended to bind suites of metal ions. The WSCP–metal complex in the retentate can be collected for proper waste management, or the binding can be reversed to recover the metal ions and recycle the WSCP. The latter option is affected by adjusting the solution conditions to release the metal ions from the polymer and performing a second PF step (diafiltration) to yield the metal ions in concentrated form in the permeate and the metal-free WSCP in the retentate.[7]

Los Alamos National Laboratory (LANL) employs an aqueous recovery system for plutonium-238 (Pu-238); this isotope is used as a heat and power source in deep space missions. The Pu-238 purification procedure involves precipitation of Pu(III) oxalate from 1–2 N nitric acid followed by neutralization of the filtrate solution with sodium hydroxide. After recovery of the hydroxide precipitate by filtration, the filtrate solution often exceeds the alpha activity limit (>4.5 mCuries/L) required for disposal of the solution to the Laboratory's waste-water treatment facility.[11] A PF process has been implemented to recover the Pu-238 from this process stream for proper waste management.[12]

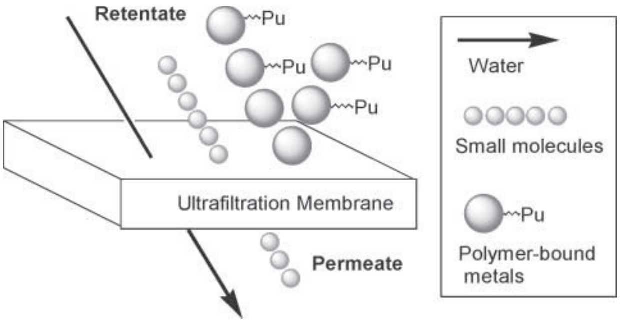

Figure 1. Polymer filtration depends on an ultrafiltration membrane that retains higher molecular weight species, such as Pu(IV) bound to a water-soluble chelating polymer, while allowing water and smaller molecules to pass. (View this art in color at www.dekker.com.)

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Polyethylenimine (PEI) is a useful scaffold for a variety of WSCPs. PEI is a polymerized aziridine with a ratio of primary to secondary to tertiary nitrogens of 1 : 2 : 1 (Fig. 2) and it has been purified to a minimum molecular weight cut off of 30,000.[13] Appending PEI primary nitrogens with amide linkages to 2,3-

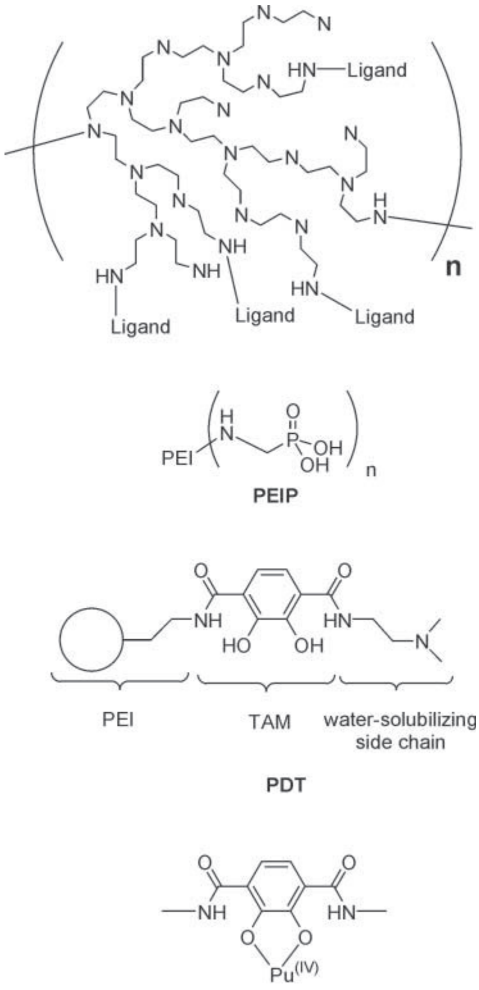


Figure 2. The water-soluble chelating polymer consists of PEI that has been functionalized on the primary amines with 2,3-dihydroxyterephthalamides. The dimethylaminoethyl side chain allows the WSCP to remain soluble throughout the pH range and in solutions of varying ionic strength. Upon deprotonation of the ligand, Pu(IV) is bound by the catecholate oxygens.

dihydroxyterephthalamides (TAM) forms a WSCP. 2,3-Dihydroxyterephthalamides were chosen for study as potential chelating agents for plutonium recovery for several reasons. Derivatives of catechol have been extensively investigated because of the extraordinarily strong complexes they form with high valent metal cations. The archetype of such ligands is enterobactin(ent), a naturally occurring Fe(III) chelator. Enterobactin contains three catecholamides, and the overall formation constant of the $[Fe(ent)]^{3-}$ complex is 10^{49}.[14] A large contributor to their high stability is the strong electrostatic interaction between the double negatively charged ligand and the large positive charge on the metal. Thus, the TAMs have a high affinity for metal ions such as Fe(III), Ce(IV), Pu(IV), and, Th(IV), and they show substantial selectivity for Pu(IV) over Am(III) and the trivalent lanthanides.[15−21] These large formation constants allow the TAMs to chelate metal ions when they are present at very dilute concentrations. The second amide of the TAM can be functionalized with a variety of groups, which helps maintain the water solubility of the WSCP throughout the processing pH range, in higher ionic strength solutions, and after metal-ion binding.

Lowering the pH to release the bound metal ions can recycle WSCP used in a PF process. In some cases, the metal-ion formation constants are so high that even high acid does not readily release the metal ions. In these cases, it may be more desirable to oxidatively destroy the polymer to recover the concentrated metal ions.

Prior work examined WSCP containing phosphonic-acid-type chelators (see Fig. 2) for recovering plutonium and americium.[12] Since the phosphate produced by the oxidative destruction of these types of polymers interferes with the subsequent plutonium recovery processes, there may be an advantage in designing ligands that can be oxidized to volatile carbon, nitrogen, and oxygen products. The synthesis of a TAM-type of a WSCP and its plutonium and americium binding studies are presented and discussed in this article.

EXPERIMENTAL

General

All reagents and solvents were purchased from Aldrich Chemical Company (Milwaukee, WI) or Fisher Scientific (Pittsburgh, PA) and were used as purchased. Solvents were dried over activated alumina and stored over 4-Å molecular sieves. Reactions were carried out under argon. Thionyl chloride was purified by distillation from triphenyl phosphite. Water was distilled and further purified by passing it through a Millipore (Bedford, MA) Milli-Q cartridge system (resistivity 18 MΩ). Thin layer chromatography

(TLC) was performed using alumina-backed silica plates and visualized with a 254-nm UV lamp. All organic extracts were dried over $MgSO_4$, and solvents were removed under vacuum with a rotary evaporator. ^1H and ^{13}C NMR spectra were obtained on a Bruker (Bellerica, MA) DRX500 (500 MHz) or Bruker AMX400 spectrometer (400 MHz). NMR samples were taken in $CDCl_3$ or D_6-DMSO. Microanalyses were performed by the Microanalytical Services Laboratory in the College of Chemistry, University of California, Berkeley, CA. Compounds **1** and **3** were prepared as previously reported.[22,23] The polymer filtration unit consisted of a QuixStand Benchtop system fitted with a feed reservoir and a 30,000 MWCO filtration membrane (Xampler UFP-30-C4A, AG Technology Corporation, Needham, MA) and a peristaltic pump (EasyLoad Masterflex, Cole Parmer Instrument Co., Niles, IL). Pu-238 and Am-241 stock solutions in 8-M HNO_3 were obtained from Los Alamos analytical supplies, as previously reported.[12] Pu(III) preparation was performed as previously described.[11] An Orion, (Boston, MA) EA 940 meter with a semi-micro, nonrefillable pH combination electrode was used for making pH measurements. Ultrafiltration cartridges were dead-end Amicon-Centricon-10 units (Millipore, Bedford, MA). A Beckman (Fullerton, CA) Model TJ-6 centrifuge with a fixed-angle rotor was used to produce permeates for the metal-binding studies. Specific alpha activities of aqueous solutions, 0.010 to 1.0 mL aliquots, were measured by liquid scintillation counting (LSC) by adding weighed aliquots to a tared vial containing 20 mL of Ultima Gold (Packard, Downers Grove, IL) scintillation cocktail and counting on either a Packard (model Tri-Carb 2200CA) or a Beckman (model LS6000) liquid scintillation counter. Net counts were obtained by subtraction of the cpm of a background sample consisting of 20 mL of Ultima Gold scintillation cocktail.

Polymer Synthesis

Bn-DMETAMthiaz, 4

N,*N*-Dimethylethylenediamine (0.14 mL, 1.25 mmol) dissolved in 100 mL of CH_2Cl_2 was added dropwise over 20 hours to compound **3** (1.4 g, 2.5 mmol) dissolved in 350 mL of CH_2Cl_2. This reaction product was evaporated to 75 mL and washed 2 times with 50 mL of 1-M KOH/brine, dried over $MgSO_4$, filtered, and vacuum rotary evaporated to a yellow oil. The crude oil was chromatographed on a silica gel column and the excess **3** was eluted with CH_2Cl_2/1% MeOH and the product **4** was eluted with 5% MeOH. The fractions containing compound **4** were combined and vacuum rotary evaporated yielding a yellow oil (0.35 g, 51% yield). ^1H NMR (300 MHz)

δ: 2.13 (singlet, 6H, $N(CH_3)_2$), 2.33 (triplet, 2H, CH_2), 2.92 (triplet, 2H, CH_2), 3.42 (triplet, 2H, CH_2), 4.36 (triplet, 2H, CH_2), 5.10 (singlet, 2H, CH_2), 5.13 (singlet, 2H, CH_2), 7.21 (doublet, 1H, CH), 7.90 (doublet, 1H, CH), 8.06 (broad triplet, 1H, NH).

Bn-PEIDMETAM, **5**

PEI [minimum molecular weight cut off (MWCO): 30,000; 0.109 g] dissolved in 20 mL of CH_2Cl_2 was added slowly to ligand **4** (mole ratio of 1 : 1 of **4** to primary nitrogens in PEI) dissolved in 20 mL of CH_2Cl_2. After stirring for 12 hours, 2 mL of MeOH was added to the cloudy pale yellow solution to complete the dissolution. After stirring for 3 days, only a faint yellow color remained. The reaction mixture was evaporated, dissolved in 250 mL dd H_2O, and all small molecule impurities were removed by diafiltration (30,000 MWCO).

PEIDMETAM (PDT), **6**

Polymer **5** (1 g) was dissolved in 25 mL of glacial acetic acid and 25 mL of 48% HBr under N_2, stirred for 5 days, and evaporated to an off-white solid. Upon addition of dd H_2O, the solution turned a pale pink, indicating the presence of Fe(III). EDTA was added and the pH was adjusted to 3 to remove the Fe(III) from the WSCP. Diafiltration (30,000 MWCO) separated the Fe(EDTA) complex and other small molecule impurities from the polymer. A clear, light brown film resulted upon vacuum rotary evaporation. Elemental analysis of PDT: C 36.01%, H 7.09, N 11.40, C/N ratio is 3.159 (PEI has a calculated elemental analysis of C 24.022%, H 5.039%, N 14.007%, C/N ratio is 1.715); (anticipated C/N ratio of 2.856 calculated from 1 TAM added for every primary nitrogen in PEI).

Metal-Binding Studies

Preparation of PDT Stock Solution

A 1% stock solution of PDT was prepared by dissolving 0.102 g of PDT in 10.106 g of H_2O. This solution was filtered through 5.0-, 0.45-, and 0.22-micron filters and used as the stock for all of the experiments.

Pu(IV) and Am(III) Binding Experiments

A 0.01% solution of PDT was prepared by diluting 0.100 mL of the stock solution with 10 mL of 0.1 M $NaNO_3$. To this solution was added 0.05 mL of Pu(IV) solution or 0.20 mL of an Am(III) solution; the final "feed solution" activity was ~35,000 counts per minute per gram (cpm/g). The stirred feed solution was equilibrated for at least 15 minutes, the pH was recorded, and a weighed aliquot (0.1 mL) removed for LSC analysis. Centrifuging 1.0 mL of the feed solution at 4000 rpm for 25 minutes in a 10,000 MWCO Centricon-10 tube produced a permeate sample; a weighed aliquot was obtained for LSC analysis. Experiments were performed as a function of pH by adding small aliquots ($\leq$0.010 mL) of 1-M or 10-M NaOH or 1-M or 16-M HNO_3 to the stirred feed solution. A semimicro pH electrode was used to monitor the pH of the stirred feed solution. Aliquots of the feed solution were removed after obtaining stable pH readings; up to 8 data points at different pH values were obtained in this manner. Similar experiments were performed with 0.001% and 0.1% PDT solutions.

Pu(III) Binding

The experiment was conducted in the same manner as just described except that the feed solution was prepared from 5 mL of 0.1-M $NaNO_3$ and 5.0-mL of a Pu(III) solution that was 0.5-M HAN and 0.5-M HNO_3. The final feed solution activity was ~35,000 cpm/g.

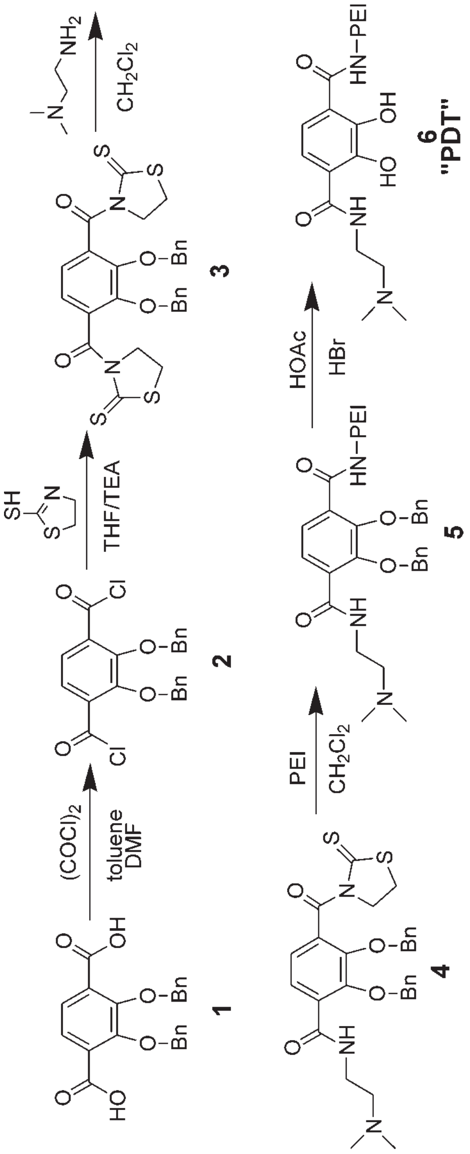
Dissolution of Pu(IV) in a Basic Solution

Two 10-mL solutions of 0.1-M $NaNO_3$ were spiked with 0.05 mL of Pu(IV) and adjusted to pH 12.3 with NaOH. Aliquots of the solutions were taken at regular intervals for LSC over 4 hours. At 4 hours, one of the solutions was made 0.01% in PDT; sampling of both solutions then continued.

RESULTS AND DISCUSSION

WSCP Synthesis

PDT was synthesized by first preparing the protected TAM portion using reported methods, attaching the dimethylethylenediamine side chain, coupling to PEI, then deprotecting the catecholate oxygens (Sch. 1).[22,23] 2-Mercaptothiazoline was chosen as the activated leaving group for the benzyl-protected **3** for several reasons. The 2-mercaptothiazolide leaving group is only reactive toward primary amines, is bright yellow when attached to the ligand, and can be used in a variety of solvents including alcohols and water. Slow addition of a substoichiometric amount of dimethylethylenediamine to a solution of **3** encourages the formation of the mono-substituted **4**. The excess, unreacted **3**, can then be recovered and reused. The ^{1}H NMR data was consistent with the proposed



Scheme 1. The synthesis of PDT is accomplished from known starting materials.

structure of **4**. Compound **4** was then coupled to PEI in $CH_2Cl_2/MeOH$ to give polymer **5**. The progress of the reaction was monitored by the disappearance of the yellow color of **4**. Use of the 2-mercaptothiazolide leaving group ensures the functionalization of only the primary PEI amines. Since one out of every four nitrogens is a primary nitrogen in PEI, the TAM loading level is approximately 1/4. Since **5** is a water-soluble polymer, the small molecular impurities were removed by diafiltration with water. Crude PDT was then obtained by removing the protecting benzyl groups of **5** with HBr/HOAc. After neutralization of the solution and purification by diafiltration, the PDT had a pale pink color, indicating that traces of Fe(III) contamination were acquired from the glassware or other reagents. The Fe(III) was removed from PDT by adding EDTA and adjusting the pH to approximately 3; under these conditions, Fe(III) is preferentially chelated by EDTA. The Fe(EDTA) complex was removed by diafiltration using water as the washing solution (usually five to six volume equivalents) until all salts and small molecules had been removed from the PDT. The final solution was lyophilized to afford PDT as an off-white powder.

Metal-Binding Studies

A solution of 0.01% PDT in 10 mL of 0.1-M $NaNO_3$ was used for most of the metal-ion retention experiments. Before any metal-binding experiments were performed with this solution, a qualitative pH titration from pH 1.5 to 12.5 was conducted to determine solubility characteristics of PDT. PDT was found to be soluble throughout the pH range and in solutions of differing ionic strength. This was an important issue since similar WSCP that contained sulfate-substituted TAMs instead of the dimethylethylenediamine side chain had limited solubility (unpublished observations).

For the metal-binding studies, the 0.01% PDT/0.1-M $NaNO_3$ solution was spiked with an appropriate amount of radionuclide, stirred for 15 minutes to equilibrate, the pH recorded, and then two samples were removed. The first sample, a weighed aliquot ($\sim$0.1 g), was taken to determine the specific activity (cpm/g) of the unfiltered PDT solution by liquid scintillation counting. In processing terms, this is commonly designated the "feed" sample. The second sample, $\sim$1 mL, was used to generate "permeate" sample by polymer filtration through a Centricon-10 unit. A Centricon-10 unit consists of two test-tube shaped parts that hold approximately 2 mL each. The two pieces snap together and are separated by a 10,000 MWCO membrane filter attached to the bottom of the top half.[7,12] A 1-ml feed sample placed in the top half of the unit produced $\sim$0.8 mL of permeate in the bottom half of the unit after centrifuging for 30 minutes at 4000 rpm. The specific activity of the weighed permeate was measured. After the initial feed and permeate samples were obtained, the PDT solution was adjusted to seven sequentially higher pH values by small additions of NaOH or HNO_3. The sampling for feed and permeate samples was then repeated for each pH point. A semimicro pH electrode monitoring the stirred PDT solution indicated that the pH came to equilibrium within several minutes.

The distribution coefficients (D), as a function of pH, were determined from the specific activities of the corresponding feed and permeate LSC counts. The alpha peaks were well shaped with no noticeable chemical or color quenching. The amount and percent plutonium bound to the WSCP are given by Eqs. (1) and (2).[12]

$$\left(\frac{\text{cpm}}{\text{g}}\right)_{\text{bound Pu}} = \left(\frac{\text{cpm}}{\text{g}}\right)_{\text{feed Pu}} - \left(\frac{\text{cpm}}{\text{g}}\right)_{\text{permeate Pu}} \tag{1}$$

$$\%\text{bound Pu} = \left[\frac{(\text{cpm/g})_{\text{bound Pu}}}{(\text{cpm/g})_{\text{feed Pu}}}\right] \times 100 \tag{2}$$

The distribution coefficient (D) is described by Eq. (3):

$$D = \left[\frac{(\text{cpm/g})_{\text{bound Pu}}}{(\text{cpm/g})_{\text{permeate Pu}}}\right] \times \left(\frac{\text{mL}}{\text{g}}\right)_{\text{phase ratio}} \tag{3}$$

The phase ratio is the ratio of the mL of solution to the grams of WSCP in that solution. In the 0.01% PDT solution there are 10 mL of H_2O to 0.001 g PDT, thus the phase ratio is 10,000.

The Pu(IV) binding experiment was conducted twice from pH 1.5 to 11.4. Since the TAM catecholate protons have pK_a values of 6.2 and 11, it would be expected that the distribution coefficients would increase as a function of pH. This was the observed trend, however, the ligand also functions well at low pH values (Fig. 3). The highest D value was 4.8×10^6 at pH 11.4, corresponding to 99.8% bound. At pH 4.5 the observed D value was equal to 1.3×10^6 (99.3% bound). Even at pH 2.9, strong binding of Pu(IV) was observed, with a D equal to 1×10^5.

These data can be directly compared to PEIP, the phosphonic acid-based WSCP currently in use at LANL.[12] At pH 2, PEIP has a D of 5.0×10^4 (98% bound), which increased to 2.5×10^6 (99.97% bound) by pH 6. Thus, under similar conditions, PDT is not as effective in the lower pH region, but equally effective at higher pH for Pu(IV) binding.

The selectivity of TAMs for high valent metal cations is seen by comparing these Pu(IV) results to the Am(III) binding results (Fig. 4). Am D values are relatively flat from pH 2 through pH 7 ($\sim 10^3$, 14 to 30% bound) and then increase with increasing pH between pH 7 and 9. The D value at pH 10.9 is 2.1×10^6 (99.5% bound), comparable with Pu(IV), and the largest

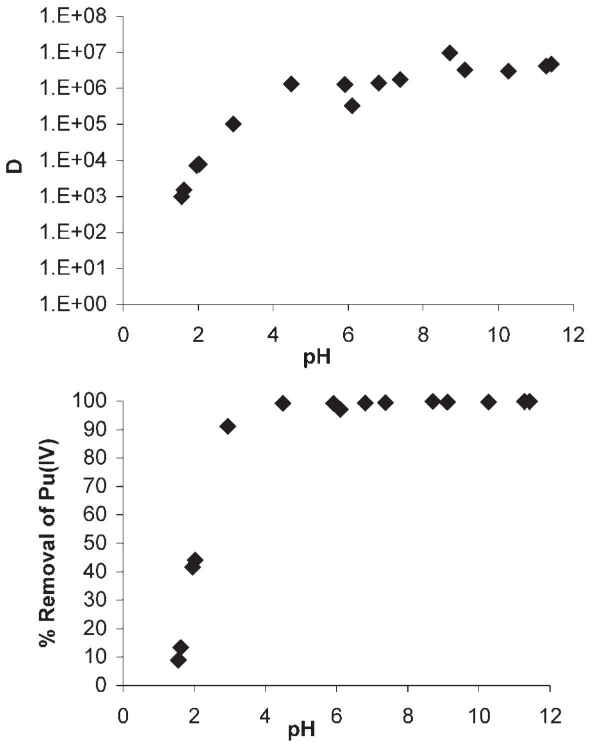


Figure 3. Plot of *D* vs. pH (top) for the uptake of Pu(IV) by PDT. The same data are plotted as percentage extraction vs. pH (bottom).

difference between the two metals is seen at pH 4.5, where *D* is 1.6×10^3 for Am(III) (14% bound) and 1.3×10^6 for Pu(IV) (99.3% bound). The discrimination of PDT between Am(III) and Pu(IV) is in contrast with PEIP, which does not discriminate between the trivalent and tetravalent actinides.[12] The low Am(III) binding between pH 2 and 7 is comparable to that observed for the PEI backbone polymer, which binds less than 2% of the Am(III) at pH 2 and 25% at pH 6.[12]

For an 8-coordinate complex of a bidentate ligand, the complexation reaction should be fourth order in ligand concentration, while it should be first order for an octadentate ligand. For a polymer with n appended bidentate ligands, the complexation reaction should be of order $(4/n)$, which approaches zero as n is increased. To test this prediction, the concentration of PDT was varied to examine the effect on Pu(IV) binding. The typical experiment involved 0.01% PDT, and it was found that varying the concentration an order

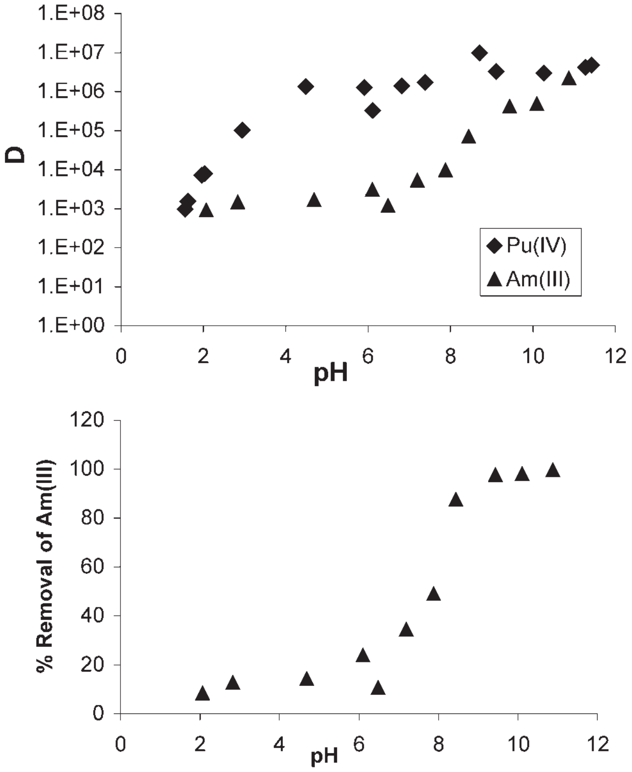


Figure 4. A comparison of Am(III) (triangles) and Pu(IV) (diamonds) uptake by PDT is shown in the plot of *D* vs. pH (top). The relation of *D* to percentage uptake for Am(III) is shown in the plot (bottom).

of magnitude in either direction to 0.1% and 0.001% had little effect on *D* values (Fig. 5). The 0.01% polymer solution was slightly better at removing Pu(IV) than the 0.1% polymer solution, which may be related to the critical micelle concentration (CDC) issues.[13] This observation is similar to what has been observed in previous binding studies with water-soluble chelating-polymers containing phosphonic acid ligands.[12]

The PDT-WSCP is being evaluated to remove plutonium from process streams resulting from the purification of Pu-238; LANL produces this plutonium isotope for space power applications. This process stream contains other processing chemicals such as hydroxylamine nitrate (HAN) used for the reduction of Pu(IV) to Pu(III) and residual oxalate from the precipitation of plutonium(III) oxalate. Previous work with systems containing Pu(III) and

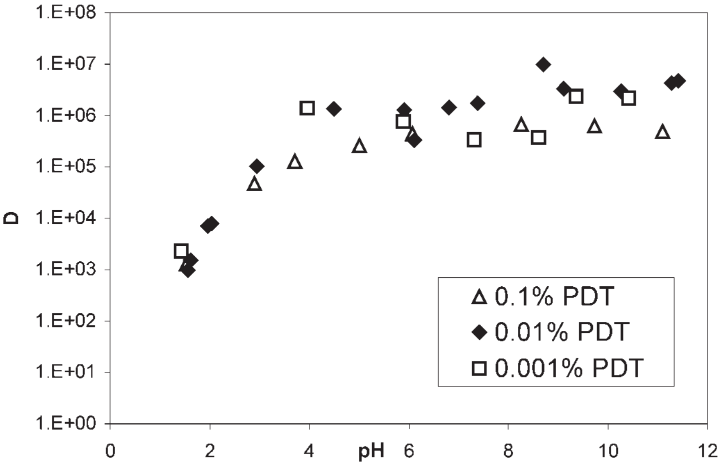


Figure 5. The graph of *D* vs. pH for Pu(IV) uptake with concentrations of PDT varying from 0.1% to 0.001%.

catecholate ligands indicated that Pu(III) was quickly oxidized to Pu(IV); the oxidation driven by the high stability of the higher oxidation state complex.[19] Although PDT efficiently sorbs Am(III), it was necessary for the intended application to see if Pu(III) could be bound by the PDT chelating polymer in the presence of a large excess of HAN. Pu(III) was prepared by reducing Pu(IV) in 0.25-M HAN, the concentration of HAN found in the process stream. The plutonium distribution coefficients between PDT and this solution are shown in Fig. 6. This figure compares these distribution coefficients to those of Pu(IV) and Am(III). The similarity of the “Pu(III) data” to the Pu(IV) data suggests that plutonium is complexed by PDT as Pu(IV) even in the presence of a large excess of HAN.

Pu(IV) is known to polymerize and adsorb to glass surfaces in neutral to basic solutions, much more than Am(III). Since these absorption effects could compromise our results, we examined the long-term behavior of plutonium in our PDT-containing feed solutions and found that the Pu-specific activity remained constant over time. This Pu(IV) solubility was true across the pH ranges studied, indicating that the PDT maintained Pu solubility even in basic solutions. In a more rigorous test, an experiment was conducted to see if PDT could solubilize adsorbed/polymerized plutonium. This experiment was done by preparing two Pu(IV)/0.1-M $NaNO_3$ solutions and adjusting to pH 12. Without PDT present there was a decrease in the specific activity of these solutions with time. Figure 7(a) illustrates this decrease for one of the

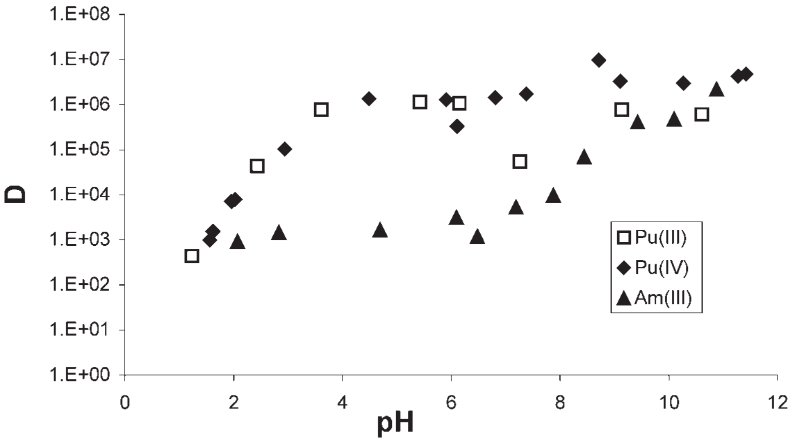


Figure 6. The graph of *D* vs. pH for the uptake of Pu(III) (squares) in the presence of HAN compared with Am(III) (triangles) and Pu(IV) (diamonds).

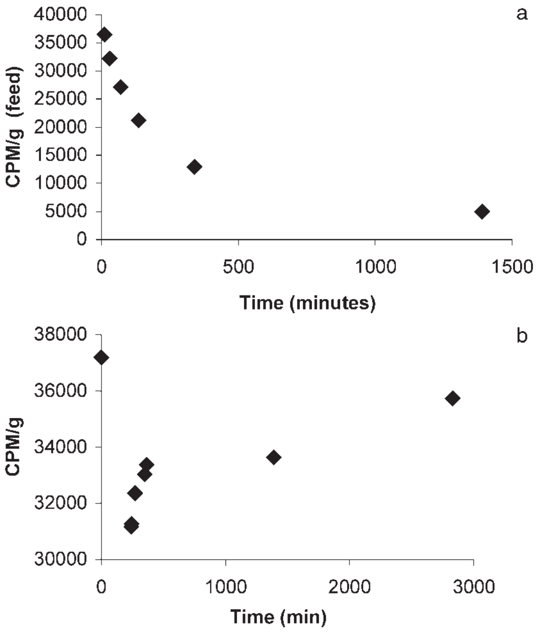


Figure 7. The graph on the top (7a) shows the decrease of cpm over time of a basic Pu(IV) solution. The graph on the bottom (7b) illustrates the increase in cpm of a basic Pu(IV) solution after addition of TAMs.

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solutions; almost half of the activity was removed from the solution in 200 minutes. After 4 hours, PDT was added to one of the solutions. The specific activity of the feed solution slowly recovered to normal after 2 days, indicating that PDT can solubilize the Pu(IV) that was adsorbed to the glass surface [Fig. 7(b)].

A series of blank ultrafiltration studies of tracer Am(III) and Pu(IV) were previously reported.[12] Though there was some retention of the metal ions in the absence of chelating polymer, the retention was less than in the presence of the chelating polymer. Metal removal was both pH and ionic-strength dependent; greater removal was observed at higher pH values and lower ionic strength and Pu retention was greater than Am retention. Blank studies have to be interpreted carefully because condensation of hydrolyzed metal ions such as Pu can take time to reach equilibrium. Colloidal material resulting from the hydrolysis can eventually grow to sizes removed by an ultrafilter and a variety of factors, such as temperature, ionic strength, and presence of the chelating polymer, can influence the condensation reaction. As observed above, the TAMs chelating groups on the polymer can suppress Pu polymerization reactions and can even redissolve colloids and precipitates.

CONCLUSION

WSCP consisting of a PEI backbone, TAM chelators, and diamine modifers were developed to remove Pu(IV) from a LANL Pu-238 process stream. The TAMs were functionalized to retain the water solubility of the polymer while providing a chelator that can be totally oxidized to gaseous C, H, and N products. The chelator's high distribution coefficients for Pu(IV) are advantageous for dilute process streams with variable plutonium concentrations and are effective across a wide pH range. In addition, if plutonium is present as Pu(III), the high stability constant of the Pu(IV)/TAM complex drives the oxidation of Pu(III) to Pu(IV); this oxidation occurs even in the presence of a large excess of HAN. TAM chelators can absorb Am(III) efficiently. However, their affinity for Pu(IV) gives the chelator some selectivity of Pu over Am, especially in the pH 3 to 9 range. These WSCP based on TAMs should be easily recycled since Pu(IV) has low binding to the TAM chelator at lower pH values, which may possibly eliminate the need for polymer degradation by oxidation. These versatile derivatives of PEI are well suited for the LANL Pu-238 process stream and could be useful for other aqueous streams as well.

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