

## Redox speciation of plutonium

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Knowledge of the oxidation state distribution of plutonium in natural waters is necessary in modeling its behavior in environmental systems. The redox speciation of plutonium is complicated by such effects as hydrolysis, complexation, disproportionation, solubility, and redox interchange reactions. The insolubility of  $\text{Pu}(\text{OH})_4$  is often the limiting factor of the net solubility of plutonium in oxic natural waters where  $\text{Pu}(\text{V})\text{O}_2^+$  is the most stable oxidation state. Perturbations to the oxidation state speciation due to the complexation chemistry of the different oxidation states of plutonium and to the insolubility of plutonium(IV) in neutral aquatic systems are discussed. The merits and limitations of some chemical separation techniques used to study redox speciation of plutonium are presented, and recommendations made for obtaining reliable oxidation state distribution data.

### Introduction

Although approximately 17 tons of  $^{239}\text{Pu}$  were made in the Oklo natural reactors<sup>1,2</sup> from neutron capture by natural uranium and subsequent  $\beta$ -decay, its half-life of  $2.41 \cdot 10^4$  years has resulted in the disappearance of this material from the environment. Except for traces of  $^{244}\text{Pu}$  ( $T_{1/2} = 8.05 \cdot 10^7$  y) remaining from primordial times,<sup>3,4</sup> the plutonium present in the environment has been introduced in the last 50 years by human activities. Releases from nuclear processing and from tests for military purposes are the primary sources. An estimated three to five thousand kilograms of plutonium (as of 1985) has been dispersed as a result of nuclear detonations.<sup>5,6</sup>

Table 1 lists the transuranium (TRU) nuclides present in the environment and their concentrations in seawater and sediments.<sup>7,8</sup> Plutonium and neptunium are the most abundant in seawater and are present in comparable concentrations, while more plutonium is present in marine sediments. The strong tendency toward precipitation and sorption shown by plutonium reflects the importance of such processes in the redox behavior of plutonium.<sup>8–11</sup>

Many oxidation state speciation studies involving plutonium have been performed for fresh- and saltwater systems, and the following brief description of natural waters is useful in understanding potential perturbations to the oxidation state distribution. In such waters, processes commonly reach a steady state rather than true equilibrium, further, the concentrations of the most abundant inorganic salts remain nearly constant.<sup>12</sup> The most abundant cations in oceanic waters are  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ , and  $\text{Ca}^{2+}$ , while  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-} + \text{HCO}_3^-$ ,  $\text{Br}^-$ , and  $\text{F}^-$  are the major anions.<sup>12</sup> Figure 1 presents a Pourbaix diagram ( $E_H$  vs. pH) in which the measured  $E_H \approx 0.8$  V at  $\text{pH} \approx 8$  (e.g., seawater) is due to the  $\text{O}_2/\text{H}_2\text{O}$  couple.<sup>11,13,14</sup> However, the redox ability of aquatic systems seldom is described adequately by the measured  $E_H$  values, and more details of the solution chemistry must be understood to predict redox speciation with confidence.<sup>11,12,15</sup>

Due to local environmental influences, freshwater systems have wider variations in pH and  $E_H$ . For the pH range 4–10, oxic surface waters have measured  $E_H$  values in the range 0.2–0.6 V, and for subsurface anoxic waters, –0.4–0.0 V.<sup>5</sup> Freshwater systems generally have lower inorganic anion contents, but may possess unusually high concentrations of organic materials (i.e., peat bogs, darkwater systems, etc.) which may have both complexing and redox behavior.

Naturally occurring organic ligands, such as the humic and fulvic acids, can markedly influence plutonium redox speciation by complexation assisted reduction of  $\text{Pu}(\text{VI})\text{O}_2^{2+}$  to  $\text{Pu}(\text{V})\text{O}_2^+$  and  $\text{Pu}(\text{IV})$ , the extent of which can vary depending on solution conditions.<sup>5,8,11,16</sup> Plutonium(IV) in seawater is strongly hydrolyzed, and the  $\text{Pu}(\text{OH})_4$  species may sorb to colloids, humates, inorganic minerals, or combinations thereof.<sup>5,8,10</sup> Photolytic degradation of humic substances in surface waters produces micromolar concentrations of  $\text{H}_2\text{O}_2$  which also can perturb the redox behavior of plutonium.<sup>11</sup>

In analyses of plutonium in natural waters, most samples are filtered to remove humic substances and suspended particulates prior to analysis with the assumption that the plutonium retained by the filter is  $\text{Pu}(\text{IV})$ , present either as a colloidal hydrous polymer or sorbed to humates. Such removal of  $\text{Pu}(\text{IV})$  can perturb

Table 1. Transuranic actinide concentrations (in mol/kg sample) in marine environments\*

Nuclide	Seawater	Sediment
$^{237}\text{Np}$	$2 \cdot 10^{-14}$	$2 \cdot 10^{-11}$
$^{238-241}\text{Pu}$	$1 \cdot 10^{-14}$	$5 \cdot 10^{-10}$
$^{241}\text{Am}$	$4 \cdot 10^{-17}$	$4 \cdot 10^{-12}$
$^{244}\text{Cm}$	$3 \cdot 10^{-22}$	$3 \cdot 10^{-21}$
Total	$3 \cdot 10^{-14}$	$5 \cdot 10^{-10}$

\*Values for northern hemisphere. Adapted from References 7 and 11.

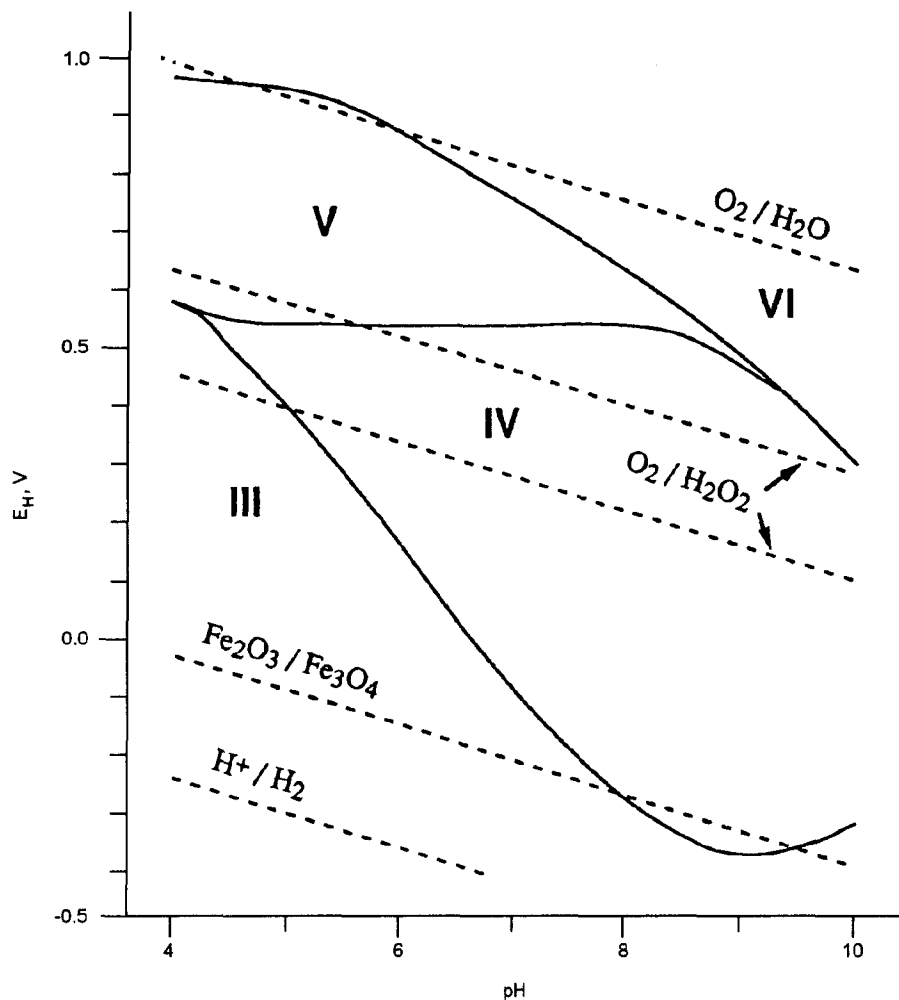


Fig. 1. Pourbaix diagram for plutonium in a low ionic strength system at low total plutonium concentrations, adapted from Reference 5. The system is assumed to be in equilibrium with atmospheric carbon dioxide, and complexation constants ( $Pu(OH)_4^-$  has not been included) from References 5 and 13

the oxidation state distribution of the dissolved plutonium; however, not filtering may introduce error if the conditions (pH, etc.) of the speciation analysis cause release of Pu(IV) to the solution. The influence of humate interactions on actinide speciation has been discussed elsewhere<sup>5,6,8,11,16</sup> and is reviewed only briefly in this paper.

An understanding of plutonium oxidation state distribution is of interest in estimating the residence time of plutonium in marine systems. Redox speciation is also important in geochemical modeling concerning possible releases associated with the long term storage of radioactive wastes. The latter requires detailed predictions of oxidation state distributions in order to model environmental migration, as this is strongly dependent on the oxidation state of plutonium. This paper discusses some important aspects of plutonium chemistry in aquatic systems with emphasis on how they relate to redox speciation experiments. The limitations and advantages of

some chemical separation methods for plutonium redox speciation are discussed, and recommendations on their usage are made.

## Discussion

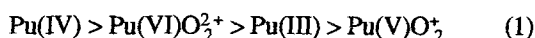
### *Chemistry of plutonium in aquatic systems*

The relationship between redox activity and complexation in plutonium chemistry presents a challenge to scientists attempting to model plutonium redox speciation in complex environmental matrices. The oxidation state distribution of plutonium in natural waters can be affected by a number of variables including  $E_H$ , hydrolysis, complexation, disproportionation, solubility, and redox interchange.

In general, the reduced (III, IV) oxidation states of the actinides are stabilized in acidic media, while the oxidized (V, VI) states become more stable as the pH increases.

Table 2 lists the reduction potentials for plutonium cations at various pH values: the potentials have been corrected for hydrolysis.<sup>4,13</sup> The reduction potential at pH 8 for the Pu(IV)/Pu(III) couple is -0.39 V, indicating that Pu(III) would not be present in oxic seawater. These reduction potentials indicate the possibility of plutonium(IV), (V), and (VI) existing simultaneously in different concentrations in the pH range common to most natural waters.

The complexation strength of plutonium usually decreases in the order:<sup>4,8,17,18</sup>



An effective charge of  $\approx +3.2$  has been assigned to plutonium in  $\text{Pu(VI)O}_2^{2+}$ ,<sup>8,17,19,20</sup> and this supports its position in this series. This sequence of complexation strength does vary, and depends on solution conditions.<sup>4,8,17</sup>

The strong complexation of Pu(IV) and  $\text{Pu(VI)O}_2^{2+}$  can be a significant factor in redox speciation experiments involving natural waters (Pu(III) is not present in such oxic systems), as binding by  $\text{F}^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{CO}_3^{2-}$  may alter the oxidation state distribution of plutonium. An important example of such binding effects is found in the reduction of  $\text{Pu(V)O}_2^+$  to Pu(IV) in the  $\text{LnF}_3$  coprecipitation process.<sup>4,21-24</sup> In the presence of 0.5M HF, the strong complexation of Pu(IV) by fluoride and the low solubility of  $\text{PuF}_4$  ( $\log K_{sp} = -19.2$ )<sup>4,25</sup> cause reduction of approximately 20% of  $\text{Pu(V)O}_2^+$  to Pu(IV), and the extent of such reduction increases as [HF] increases.<sup>26</sup>

The pH of the solution is of prime importance as hydrolysis of polyvalent cations is extensive at naturally occurring pH values. In noncomplexing media the hydrolysis of Pu(III) occurs around pH 5, whereas hydrolysis of Pu(IV) is already significant by pH 1.  $\text{Pu(V)O}_2^+$  shows little hydrolysis below pH 9, while the greater Lewis acidity of  $\text{Pu(VI)O}_2^{2+}$  results in hydrolysis in the pH range 3-4 which is lower than for Pu(III). Under slightly acidic conditions the hydrolysis of Pu(IV) can result in formation of a hydroxy polymer which ages to the intractable oxo polymer.<sup>4,27</sup> Figure 2 shows the speciation of the Pu(IV) mononuclear hydrolysis products as a function of pH.<sup>13</sup>

Redox kinetics is another factor to consider in oxidation state speciation studies. Because only electron transfer is

Table 2. Reduction potentials of plutonium

	pH 0 <sup>a</sup>	pH 8 <sup>b</sup>	pH 14 <sup>b</sup>
Pu(IV)/Pu(III)	0.982	-0.39	-1.04
$\text{Pu(V)O}_2^+/\text{Pu(IV)}$	1.170	0.70	0.52
$\text{Pu(VI)O}_2^{2+}/\text{Pu(V)O}_2^+$	0.916	0.60	0.16
$\text{Pu(VI)O}_2^{2+}/\text{Pu(IV)}$	1.043	0.65	0.34

<sup>a</sup>Potentials from Reference 4.

<sup>b</sup>Potentials in alkaline media have been corrected for hydrolysis and are from Reference 13.

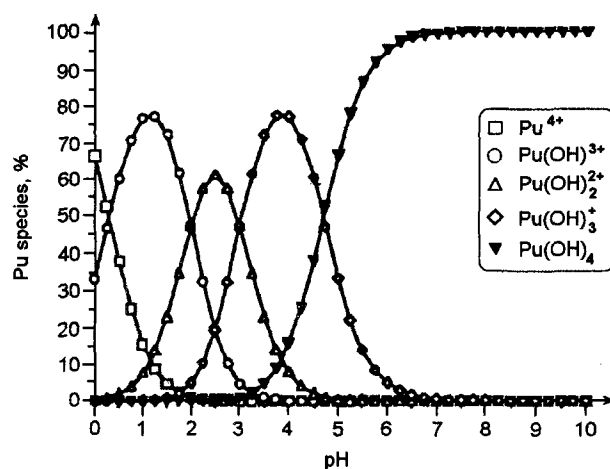
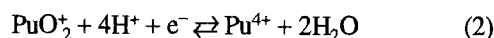


Fig. 2. Variation of mononuclear plutonium(IV) hydrolysis products as a function of pH. Stability constants taken from Reference 13

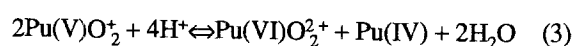
involved, oxidation or reduction reactions between the (III) and the (IV) and between the (V) and the (VI) states are rapid. However, redox between a dioxo cation and the simple Pu(III) and Pu(IV) cations, for example:



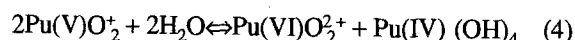
is slow due to the need to disrupt the Pu-O bonds. This example also reflects the fourth power dependence on hydrogen ion concentration in such reduction of the oxocations. This results in the increased stability of the (V) and (VI) states with increased pH.

The reduction of ca.  $10^{-9}\text{M}$   $\text{Pu(VI)O}_2^{2+}$  to  $\text{Pu(V)O}_2^+$  is 90% complete after several minutes in organic-free synthetic seawater at pH 8, while in the presence of 0.1-1.0 mg/l humic acid, 60-85% of the  $\text{Pu(VI)O}_2^{2+}$  at this concentration undergoes a two electron reduction (presumably by the hydroquinone moieties in humic acids)<sup>5,16</sup> over a period of 10-20 hours and is removed from solution as  $\text{Pu(OH)}_4$ .<sup>5,6</sup> The more weakly complexed  $\text{Pu(V)O}_2^+$  shows a much slower reduction rate. The kinetic and pH barriers to reduction of  $\text{Pu(V)O}_2^+$  and its weak complexing ability combine to result in kinetic, rather than thermodynamic control of the dissolved plutonium species in aquatic systems.<sup>6,10,11</sup>

At the plutonium concentrations typically encountered in marine systems (Table 1), disproportionation reactions are less likely than in acid solutions due to the dependence on the square of the plutonium concentration as well as a fourth power dependence on  $[\text{H}^+]$ , as in



In alkaline conditions this disproportionation can be written as:



which may represent the important disproportionation reaction in the preconcentration of slightly alkaline aquatic samples where  $\text{Pu(V)O}_2^+$  is the primary soluble species.<sup>5,8,10,11,14,28,29</sup>

In natural waters Reaction (4) is unfavorable as such disproportionation is dependent on the square of the  $\text{Pu(V)O}_2^+$  concentration and the reduction potential of the system, which favors reduction of plutonyl(VI) to plutonyl(V) (see below). However, redox speciation using instrumental techniques often requires sample preconcentration, and under conditions acidic enough to suppress precipitation of hydrolysis products Reaction (3) may occur. The disproportionation and redox chemistry of plutonium have been reviewed earlier,<sup>4,8,17</sup> as have the relation to oxidation state distribution studies.<sup>18</sup>

The Pourbaix diagram in Fig. 1 predicts that  $\text{Pu(VI)O}_2^{2+}$  should be the principal dissolved form of plutonium in oxic seawater, yet  $\text{Pu(V)O}_2^+$  has been observed as the dominant soluble species.<sup>5,8,10,11,14,28,29</sup> Reduction of plutonyl(V, VI) to plutonium(IV) can occur in natural water systems, and this has important effects on plutonium oxidation state speciation. The solubility of  $\text{Pu(OH)}_4$  is quite low, and a  $\log K_{sp} = -55 (\pm 2)$  is often quoted.<sup>8,10,13,30</sup> Using a value of  $-55$ , in a solution free of complexants at pH 8, precipitation of  $\text{Pu(OH)}_4$  is calculated to occur at  $\text{Pu(IV)}$  concentrations of  $\approx 10^{-31}\text{M}$ . Figure 3 shows the free metal ion concentrations for  $\text{Pu(III)}\text{--Pu(VI)}$  as a function of pH and illustrates the limiting solubility of  $\text{Pu(IV)}$  in aquatic systems.<sup>8-10</sup>

Due to redox reactions between  $\text{Pu(IV)}$ ,  $\text{Pu(V)O}_2^+$ , and  $\text{Pu(VI)O}_2^{2+}$  in marine systems, plutonium is continually

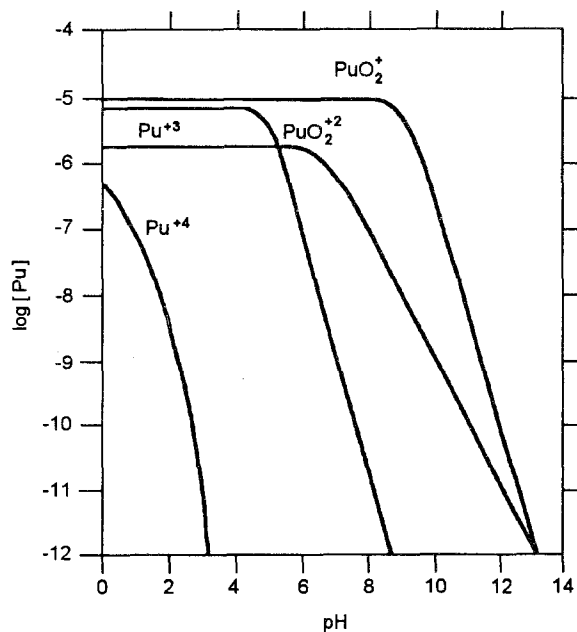


Fig. 3. Free plutonium ion concentrations as a function of pH. Adapted from References 13 and 14

being removed from solution by  $\text{Pu(OH)}_4$  precipitation and sorption of the hydrolyzed species to humates, colloids, and mineral surfaces. In fact, in most systems the concentration of sorbed  $\text{Pu(IV)}$  exceeds the concentration of  $\text{Pu(V)O}_2^+$  in solution,<sup>11</sup> as seen in Table 1. Plutonium(IV) hydroxide also "ages" to a hydrous oxide form which is less soluble so such precipitation or sorption leads to slow removal of plutonium from the solution phase over time.

#### Methods of plutonium redox speciation

The hydrolysis, complexation, redox, and disproportionation reactions of plutonium must be considered in the design or use of oxidation state speciation experiments. Despite advances in analytical techniques, for example, the low sensitivity of most spectral methods (compared to radiometric detection) necessitates sample pretreatment to concentrate the plutonium. If simple analysis of total plutonium is the objective, such preconcentration can be performed as alteration of the oxidation state distribution is of no concern. However, for measurement of the oxidation state distribution of plutonium, preconcentration is highly likely to produce significant variations in the relative concentrations of the different oxidation states.

The rapidity and selectivity offered by chemical separations are distinct advantages in oxidation state speciation, and certain separations (e.g., some solvent extraction procedures) do not require sample preconcentration or significant pH adjustment. In addition to their rapidity, the other important advantage of chemical separations with radiometric detection is that data on several and, often, all oxidation states of the actinides can be obtained at the tracer concentrations encountered in environmental samples.

Since its initial use in the isolation and purification of newly synthesized actinides, precipitation has been a versatile tool in the separation of reduced (III, IV) from oxidized (V, VI) actinides.<sup>18</sup> Two of the best known precipitation methods are the  $\text{BiPO}_4$  process<sup>4</sup> and  $\text{LnF}_3$  coprecipitation.<sup>4,21-24</sup> The  $\text{BiPO}_4$  precipitation separates  $\text{Pu(IV)}$  which can later be oxidized to soluble  $\text{Pu(VI)O}_2^{2+}$  for ease of isolation. This process was initially used by the United States for plutonium isolation from reactor irradiated uranium, but suffered from loss of uranium to the waste stream and was later replaced by solvent extraction procedures.<sup>24,31</sup> Due to its effectiveness and simplicity,  $\text{LnF}_3$  coprecipitation is the best characterized of the actinide precipitation schemes. This technique exploits the strong complexation of fluoride by  $\text{An(III)}$  and  $\text{An(IV)}$ , the insolubility of the neutral fluoride compounds, and the slow redox kinetics between the reduced (III, IV) and the oxidized (V, VI) states.

An example of the use of  $\text{LnF}_3$  coprecipitation for plutonium oxidation state speciation studies has been reported for seawater samples collected near the Windscale nuclear reprocessing facility.<sup>32</sup> The addition of dichromate

to these samples oxidized Pu(III) to Pu(IV) or Pu(V)O<sub>2</sub><sup>+</sup> to Pu(VI)O<sub>2</sub><sup>2+</sup>, providing reduced (Pu(III) + Pu(IV)) and oxidized (Pu(V) + Pu(VI)) speciation data. This study did show that greater than 90% of the plutonium(IV) and (VI) sorbed to particulates in unfiltered samples could be removed by leaching in acid (0.8M HNO<sub>3</sub>, 0.25M H<sub>2</sub>SO<sub>4</sub>, and 0.5mM K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>).

A more detailed study of LnF<sub>3</sub> precipitation investigated several important variables and their influence on plutonium(V) reduction and coprecipitation.<sup>26</sup> An important finding was that increased HF concentrations led to increased sorption of Pu(V)O<sub>2</sub><sup>+</sup>, presumably as reduced Pu(IV). Approximately 10% sorption of plutonium, which was initially 100% Pu(V)O<sub>2</sub><sup>+</sup> in solution, was observed after 30 minutes in 0.26M HF, while nearly 60% was sorbed in 1.25M HF in the same time period. Complete reduction and sorption of Pu(V)O<sub>2</sub><sup>+</sup> was observed after only 5 minutes in 4.2M HF. These results reflect the need to add a stabilizing oxidant (e.g., dichromate) and/or to maintain the concentration of HF below 0.26M to minimize reduction of oxidized plutonium.<sup>8,26,28,32</sup>

Despite the limited division of plutonium into the lower (III, IV) and the higher (V, VI) states in LnF<sub>3</sub> coprecipitation, this method is useful as a confirmatory experiment accompanying more detailed oxidation state distribution studies. Moreover, it appears that with sufficient leaching time the desorption of plutonium from particulates is almost complete,<sup>32</sup> although more detailed experimental confirmation is needed.

Sorption techniques are used in actinide redox speciation as an outgrowth from studies initially aimed at understanding the partitioning of various actinides onto aquatic mineral surfaces.<sup>8,10,33,34</sup> For example, studies showing high K<sub>d</sub> values for Np(V)O<sub>2</sub><sup>+</sup> and Pu(V)O<sub>2</sub><sup>+</sup> onto carbonaterich sediments suggested the potential of these materials for separations of oxidation states.<sup>8,10,34</sup> Several speciation studies using CaCO<sub>3</sub><sup>26,28</sup> or TiO<sub>2</sub><sup>35</sup> for Pu(V)O<sub>2</sub><sup>+</sup> and silica gel<sup>26,28,36</sup> for Pu(VI)O<sub>2</sub><sup>2+</sup> have been reported. Calcium carbonate and silica gel have received the most attention because they are more selective, inexpensive, readily available, and not redox active while each sorbs a different actinyl(V, VI) cation.

Removal of Pu(V)O<sub>2</sub><sup>+</sup> from synthetic seawater<sup>26</sup> and from freshwater<sup>28</sup> samples by sorption on CaCO<sub>3</sub> relies on the strong carbonate complexation of Pu(VI)O<sub>2</sub><sup>2+</sup>, which is retained in solution. This process requires careful pretreatment of the solid prior to use to maximize the separation of Pu(V)O<sub>2</sub><sup>+</sup> from Pu(VI)O<sub>2</sub><sup>2+</sup>, and the optimized parameters include washing the CaCO<sub>3</sub> with a buffered solution at the same pH as the sample, use of a 50 g/l solid/solution ratio, and a 5–10 minute contact time.<sup>26</sup>

Sorption of Pu(VI)O<sub>2</sub><sup>2+</sup> can be achieved with silica gel that has been pretreated to minimize pH change in the sample, a 10 g/l solid/solution ratio, and 2–4 hour contact time.<sup>26</sup> Addition of untreated silica gel to synthetic seawater samples led to an appreciable decrease in pH, which is probably related to ion exchange between the silica gel and matrix cations. As with CaCO<sub>3</sub>, pretreatment

of the silica gel is necessary to avoid changes in pH which may alter the oxidation state distribution of plutonium in the sample. Lower Pu(VI)O<sub>2</sub><sup>2+</sup>/Pu(V)O<sub>2</sub><sup>+</sup> separation factors are observed with untreated CaCO<sub>3</sub> and silica gel.

Complications with sorption techniques include surface reduction of Pu(V)O<sub>2</sub><sup>+</sup> to Pu(IV) on iron containing solids<sup>8,33,34</sup> as well as nonuniform surface area of the substrate.<sup>18</sup> It is recommended that these sorption techniques be coupled with other methods to ensure reliability of the speciation data (especially for Pu(III) and Pu(IV)).

Liquid chromatographic techniques have been investigated for oxidation state speciation studies as they are a simple and effective means of separating different oxidation states. Actinide separations by ion exchange have been reviewed,<sup>37,38</sup> and plutonium speciation studies using a two-column procedure involving silica gel and a sulfonic acid cation exchange resin,<sup>39</sup> or an inorganic ion exchanger<sup>39</sup> have been reported and discussed in more detail elsewhere.<sup>18</sup> The disadvantages of chromatographic methods include the need to use quite low pH values in most separations as well as the need for sample preconcentration to allow loading on the column in a small volume.

Solvent extraction possesses several important advantages for oxidation state speciation including rapid and essentially complete separation of oxidation states, selectivity, high volume throughput capacity, and in certain cases minimal pH adjustment. The extractants tri-*n*-butyl phosphate (TBP),<sup>36</sup> di-2-ethylhexyl phosphoric acid (HDEHP),<sup>40</sup> thenoyltrifluoroacetone (TTA),<sup>41,42</sup> and dibenzoylmethane (DBM)<sup>26,43</sup> have all been employed in actinide oxidation state speciation.

TBP has been applied to oxidation state distribution studies of neptunium.<sup>36</sup> Using benzene as a diluent, a time dependent separation of NpO<sub>2</sub><sup>2+</sup> from Np(IV) and NpO<sub>2</sub><sup>+</sup> was achieved from 3M HCl in 5–10 minutes, while NpO<sub>2</sub><sup>2+</sup> and Np(IV) were separated from NpO<sub>2</sub><sup>+</sup> in 6M HCl. While no application to plutonium systems has been reported, the high acid concentrations required to effect separations with this neutral extractant may result in significant perturbation to the oxidation state distribution of plutonium.

HDEHP in toluene coupled with either 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one (PMBP) or TTA in xylene has been used for plutonium redox speciation.<sup>40</sup> The ratio of Pu(V)O<sub>2</sub><sup>+</sup> to Pu(VI)O<sub>2</sub><sup>2+</sup> measured by this solvent extraction method compared well with that determined by photoacoustic spectroscopy (PAS), although the latter had a large uncertainty due to ambiguity in peak assignments. The PAS and solvent extraction experiments were, however, performed using plutonium concentrations of approximately 10<sup>-4</sup> and 10<sup>-5</sup>M, respectively, and the extractions had to be performed at pH 0 due to the high distribution ratios of the Pu(IV), Pu(VI)O<sub>2</sub><sup>2+</sup>, and Pu(III) cations. PAS is of limited value for redox speciation of reduced plutonium, due mainly to low sensitivity as well as the very low solubility of plutonium in neutral and alkaline solutions.

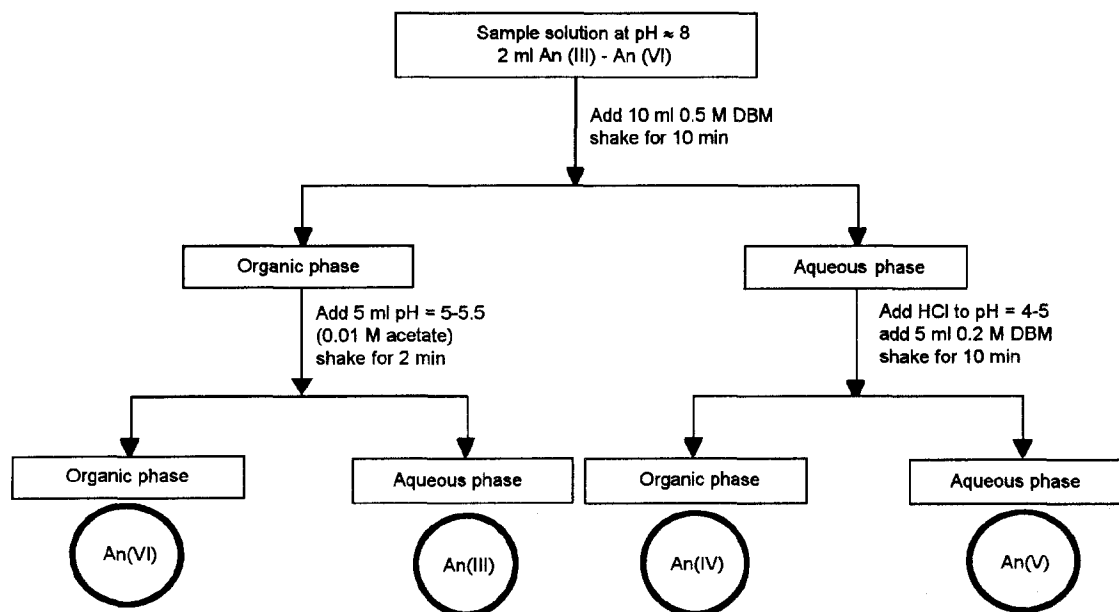


Fig. 4. Solvent extraction scheme for separating actinide oxidation states from near-neutral solutions using DBM in chloroform. Adapted from Reference 43

Solvent extraction by TTA affords oxidation state separations as a function of pH. This extraction system was initially tested using Am(III), Th(IV), Np(V)O<sub>2</sub><sup>+</sup>, and U(VI)O<sub>2</sub><sup>2+</sup> as oxidation state analogs for plutonium,<sup>41</sup> and has since been applied to mixtures of (Pu(III-VI)).<sup>42</sup> Only Pu(IV) is extracted below pH 1, which is advantageous because this pH is low enough to suppress hydrolysis of Pu(IV) and usually causes decomplexation and desorption although even this low pH may not reverse previous plutonium(IV) polymer formation.<sup>4,27</sup> Precipitation of humic acids occurs below pH ≈ 3, so adjustment to such low pH values may not release bound plutonium in unfiltered samples containing humics. Plutonyl(VI) can be extracted in the pH range 1-2, Pu(III) above pH 3, and Pu(V)O<sub>2</sub><sup>+</sup> is poorly extracted even at pH 5. Extraction by TTA has important limitations; pH adjustment may perturb the plutonium redox equilibria, and TTA has increasing aqueous phase solubility above pH 4, limiting its use to acidic media. Also, TTA solutions exposed to light prior to use have been shown to reduce Pu(VI)O<sub>2</sub><sup>2+</sup> to Pu(V)O<sub>2</sub><sup>+</sup>.<sup>11,26,44</sup>

Another redox speciation method uses solvent extraction with DBM.<sup>26,43</sup> The lower aqueous phase solubility of DBM and the pK<sub>a</sub> of 9.35<sup>(45)</sup> make it an effective extractant in the slightly alkaline region found for seawater samples. Consequently, in the DBM technique, minor pH adjustments are required after the initial separation of the (III) and (VI) from the (IV) and (V) oxidation states at pH ≈ 8. Extraction of Pu(III) and Pu(VI)O<sub>2</sub><sup>2+</sup> by DBM in benzene is complete above pH 7, leaving Pu(V)O<sub>2</sub><sup>+</sup> in the aqueous phase and Pu(IV) hydrolysis products sorbed to the walls of the glass vessel.

A process based on DBM, outlined in Fig. 4, uses chloroform as the diluent for ease of phase separation, and a glass vessel to promote sorption of Pu(IV) hydrolysis products (formation of the hydrous Pu(IV) polymer at these low concentrations is negligible).<sup>43</sup> After initial contact at pH ≈ 8, the extract containing Pu(VI)O<sub>2</sub><sup>2+</sup> and Pu(III) (if present) is contacted with an acetate buffered solution to strip Pu(III) leaving Pu(VI)O<sub>2</sub><sup>2+</sup> in the organic phase. The raffinate containing Pu(V)O<sub>2</sub><sup>+</sup> in the original glass vessel with the sorbed Pu(IV) is treated with sufficient HCl to yield a solution in the pH range 4-5 to desorb Pu(IV), which is subsequently extracted by contact with a fresh DBM solution.

No pH adjustment is required in the first DBM extraction, and, if necessary, only minor adjustment is used for mixed pairs of oxidized and reduced species that are kinetically resistant to redox interchange. When coupled with radiometric detection, the DBM extraction procedure provides a rapid and effective means of performing plutonium redox speciation studies. Spectrophotometric results using macroplutonium concentrations have confirmed the oxidation state distribution results obtained by this solvent extraction method.<sup>42</sup>

## Conclusions

In any system of oxidation state speciation, careful attention must be paid to use conditions that minimize the possibility of perturbations to the oxidation state equilibria so that accurate speciation data is obtained. Such perturbations can be induced by hydrolysis, complexation,

disproportionation (at lower pH and higher plutonium concentrations), redox interchange, and reduction by organic complexants (e.g.,  $\text{PuO}_2^{2+}$  by humics).

Numerous instrumental and chemical means exist for studying oxidation state speciation; however, each has limitations that in some way may perturb the redox equilibria of plutonium.<sup>18</sup> Instrumental techniques are mainly limited by detection sensitivity, requiring that the concentration of plutonium exceed that present in natural systems; however, macroconcentrations of plutonium may have different ratios of the oxidation states than microconcentrations. Radiometric detection coupled with fast separations and minimal change in solution conditions usually provide the most reliable speciation data.

Of the chemical separation methods for oxidation state distribution data, solvent extraction by DBM is a relatively rapid, convenient, and effective technique that minimizes perturbations to the redox speciation of plutonium. Lanthanum fluoride coprecipitation and solvent extraction using HDEHP or TTA require pH adjustment to low values and should be used with caution as primary speciation techniques, although they may be suitable as confirmatory experiments.

Due to the diverse redox and complexation chemistry of plutonium, no single oxidation state speciation method should be relied upon to provide accurate data. A reasonable approach is to use DBM solvent extraction, at or near the sample pH, with confirming data from  $\text{LnF}_3$  coprecipitation and sorption using  $\text{CaCO}_3$  or silica gel. Lanthanum fluoride coprecipitation offers simplicity and effectiveness but only yields data pertaining to reduced and oxidized pairs, and careful control of the HF concentration is required to prevent reduction of  $\text{PuO}_2^{2+}$ . However, if the sums of oxidized and reduced pairs from the DBM extraction match those obtained by  $\text{LnF}_3$  coprecipitation, the data can be assumed to be reliable. Sorption techniques are simple and fairly selective; however, they require pretreatment of the solids and take longer to equilibrate than solvent extraction methods. TTA solvent extraction is faster than that of DBM and has merits similar to  $\text{LnF}_3$  coprecipitation in that the low pH, while a potential perturbation to the redox equilibria, may allow release of Pu(IV) from naturally occurring ligands.

In summary, plutonium oxidation state distribution studies should employ at least two corroborating chemical separation methods, one near the sample pH and another at sufficiently low pH to induce plutonium release from matrix ligands. If the results from these independent experiments agree within statistical limits the oxidation state distribution can be considered reliable.

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