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Journal:	<i>Environmental Science: Processes &amp; Impacts</i>
Manuscript ID	EM-CRV-08-2017-000369.R1
Article Type:	Critical Review
Date Submitted by the Author:	30-Aug-2018
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# Environmental Science: Processes & Impacts

## Critical Review

### Plutonium environmental chemistry: Mechanisms for the surface-mediated reduction of Pu(V/VI)

Received 00th January 20xx,  
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

[www.rsc.org/](http://www.rsc.org/)

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In recent decades, interest in plutonium mobility has increased significantly due to the need of the United States, as well as other nations, to deal with commercial spent nuclear fuel, nuclear weapons disarmament, and the remediation of locations contaminated by nuclear weapons testing and production. Although there is a global consensus that geologic disposal is the safest existing approach to dealing with spent nuclear fuel and high-level nuclear waste, only a few nations are moving towards implementing a geologic repository due to technical and political barriers. Understanding the factors that affect the mobility of plutonium in the subsurface environment is critical to support the development of such repositories. The importance of redox chemistry in determining plutonium mobility cannot be understated. While Pu(IV) is generally assumed to be immobile in the subsurface environment due to sorption or precipitation, Pu(V) tends to be mobile due to its relatively low effective charge and weak complex formation. This review highlights one particularly important aspect of plutonium behaviour at the mineral-water interface—the concept of surface-mediated reduction, which describes the reduction of plutonium on a mineral surface. It provides a conceptual model for and evidence supporting or refuting each proposed mechanism for surface-mediated reduction including (i) radiolysis at the mineral surface, (ii) electron transfer via ferrous iron or manganese in the mineral structure, (iii) electron shuttling due to the semiconducting properties of the mineral, (iv) disproportionation of Pu(V), (v) facilitation by proton exchange sites, (vi) stabilisation of Pu(IV) due to the increased concentration gradient within the electrical double layer, and (vii) a Nernstian favourability of Pu(IV) surface complexes and colloids. It also provides new perspectives on future research directions.

#### Environmental Significance Statement

The actinide elements, including plutonium, carry great societal importance due to their use in medicine, power generation, national security, and nuclear waste management, but present a risk to human health and the environment due to their high toxicity and long half-lives. For example, the half-life of <sup>242</sup>Pu is 3.75 × 10<sup>5</sup> years, which means that it will be persistent in the environment for 2.63 - 3.75 million years (i.e., 7 – 10 half-lives of <sup>242</sup>Pu). For this reason, it is essential to understand the fate and transport of plutonium. The rich and complicated redox chemistry of plutonium is particularly important to study given that the oxidation state of plutonium can influence whether plutonium remains in the aqueous phase or partitions to a solid phase and thus whether plutonium is mobile or immobile. The specific phenomenon referred to as surface-mediated reduction, wherein Pu(V/VI) is reduced to Pu(IV) at the mineral surface, is only partially

understood and is important when describing plutonium behaviour at the mineral-water interface. Discerning the mechanism(s) responsible for surface-mediated reduction is fundamental to developing mechanistically-accurate conceptual models and surface-complexation models which form the basis for quantitative predictions of plutonium transport in the environment.

#### Introduction

On February 24, 1941, Glenn T. Seaborg and his research team produced the first atoms of <sup>239</sup>Pu through the neutron bombardment and subsequent β<sup>-</sup> decay of <sup>238</sup>U.<sup>1–3</sup> Within three months, they had not only demonstrated that <sup>239</sup>Pu was fissionable, but that it was more fissionable than <sup>235</sup>U.<sup>1</sup> These important discoveries, coupled with U.S. entry into World War II, significantly impacted the direction of the Manhattan Project, leading to the production, testing, and use of plutonium-based atomic weapons. Over a three-year period, approximately 12.5 metric tonnes of plutonium were produced at the Hanford Site (Richland, WA USA) for the nuclear weapons program and a similar amount was produced in the Soviet Union over a longer time period.<sup>4</sup> Lesser, though significant, amounts of plutonium were also produced in the United Kingdom, China, and France.<sup>4</sup>

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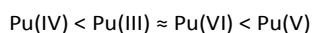
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Electronic Supplementary Information (ESI) available: aqueous plutonium speciation as a function of oxidation state and presence of carbonate. See DOI: 10.1039/x0xx00000x

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Currently, twenty isotopes of plutonium have been identified which contain between 134 and 153 neutrons. All isotopes of plutonium are considered to be anthropogenic, with the exception of ultra-trace concentrations of  $^{239}\text{Pu}$  that are found in uranium ores as a result of neutron capture by  $^{238}\text{U}$ .<sup>5</sup> As of the end of 2014, the worldwide inventory of plutonium was approximately 2600 metric tonnes<sup>6,7</sup> although less than 0.1% is estimated to have been released to the environment from global fallout and the incidents at Chernobyl and Fukushima Daiichi.<sup>8</sup> This estimate does not include environmental contamination stemming from the improper disposal of legacy wastes. The U.S. alone spends \$6.7 billion per year in environmental clean-up of their legacy waste sites. An additional \$4 billion has been spent on lawsuits related to nuclear waste storage and \$1 billion was spent responding to the incident at the Waste Isolation Pilot Plant (WIPP), in which trace amounts of plutonium (i.e., < 1/10 gram of  $^{239}\text{Pu}$ ) were released to the atmosphere.<sup>9</sup> The estimate also does not take into consideration the authorized releases of plutonium into the Irish Sea from Sellafield Ltd., which resulted in significant and widespread plutonium contamination of publicly-accessible coastal areas<sup>10–12</sup> (the reader is referred to the *Plutonium speciation in natural waters* section for further details). Regardless, there is a lack of conceptual models linking fundamental studies to observations of plutonium fate and transport at field sites.

The primary factor in determining the mobility of plutonium in the subsurface environment is its oxidation state. Plutonium is unique among the transuranic elements in that it can simultaneously exist as Pu(III), Pu(IV), Pu(V), and Pu(VI) in a single solution. This ability to exist in multiple oxidation states stems from similarities in reduction potentials and disproportionation (further discussion provided under *Aqueous plutonium chemistry*). Reduction of Pu(V) or Pu(VI) to Pu(IV) results in lower solubility and increased favourability for mineral surfaces as summarized by the actinide trend



which is based on the effective charge of each plutonium cation. The actinide trend tells us that Pu(IV) is generally assumed to be the least mobile oxidation state of plutonium and Pu(V) the most mobile. Certain caveats exist, such as sorption of Pu(IV) to mobile mineral colloids (i.e., colloid-facilitated transport), but the actinide trend remains a good rule of thumb.

Additional geochemical reactions which influence the mobility of plutonium in the environment are presented in Figure 1 and include formation and degradation of plutonium aqueous complexes, precipitation and dissolution of plutonium solid phases, and sorption and desorption of plutonium and plutonium complexes (to include ternary complex formation). The sorption of plutonium and plutonium complexes to soils, sediments, and pure mineral phases is of particular interest since interactions with these phases have the potential to

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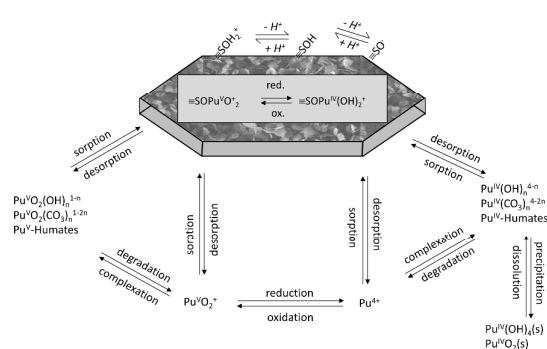


Figure 1 - Overview of potential geochemical reactions controlling the subsurface mobility of plutonium.

immobilize plutonium and therefore minimize the impact to human health. Sorption may be due to inner- or outer-sphere complexation, ion-exchange, surface (co)precipitation, or structural incorporation. One particularly important aspect of plutonium behaviour at the solid-water interface is the concept of surface-mediated reduction. This refers to the observation that plutonium added to a mineral or soil suspension as aqueous Pu(V) or Pu(VI) reduces to sorbed Pu(IV). Data consistently shows that reduction to Pu(IV) does not occur in the aqueous phase.<sup>13–25</sup> This phenomenon is only partially understood and discerning the mechanism(s) responsible for this behaviour is fundamental to developing mechanistically-accurate conceptual models describing plutonium transport in the environment.

Prior to the late 1980s, little research was performed looking at the behaviour of plutonium at the mineral-water interface. Pu(V) was known to be the dominant oxidation state of plutonium in the aqueous phase and the assumption was that it would not have significant affinity for mineral phases.<sup>26,27</sup> Keeney-Kennicutt and Morse<sup>28</sup> and Sanchez et al.<sup>13</sup> were among the first to make observations suggesting that the assumption was wrong. In particular, Pu(V) reduction was deduced from the shifting of its sorption edge to lower pH values over time and the similarity of the steady-state Pu(V) sorption edge to that of Pu(IV).

Here we present an overview of the current understanding of plutonium surface-mediated reduction organized around seven different hypotheses: (1) radiolysis at the mineral surface, (2) electron transfer via trace ferrous iron or Mn(II) at the mineral surface, (3) electron shuttling due to the semiconductor properties of the mineral, (4) disproportionation of Pu(V) at the mineral-water interface, (5) stabilisation of Pu(IV) at the mineral surface due to increased concentration gradient within the electrical double layer (EDL), (6) facilitation by proton exchange sites, and (7) reduction based on Nernstian favourability. In general, the topic of ion adsorption onto surfaces is known to be dependent on a wide range of variables, with respect to the ion's solution chemistry,

specifics of the surface, and how the two interact. The result is a multifaceted chemistry that has been the subject of a wide range of publications and excellent reviews including numerous book chapters.<sup>3,29–34</sup> The specific focus on plutonium interactions with mineral surfaces is particularly interesting because of the complexity of its solution chemistry even in the absence of a surface.

### Aqueous plutonium chemistry

The plutonium species and complexes present in the aqueous phase influence if and how plutonium will sorb to a solid phase. This section will discuss the complicated redox chemistry of plutonium, the disproportionation of Pu(IV) and Pu(V), solubility, colloid formation, and interactions between plutonium aqueous species and environmentally-relevant ligands.

Pu(III) and Pu(IV) exist as the aquo ions  $\text{Pu}^{3+}$  and  $\text{Pu}^{4+}$ , respectively, and retain their overall formal charge. However, Pu(V) and Pu(VI) form the nearly linear dioxo cations  $\text{PuO}_2^+$  and  $\text{PuO}_2^{2+}$ , respectively. The formation of these axial oxygen bonds on Pu(V) and Pu(VI) lowers their effective charges. Choppin and Rao<sup>35</sup> report an effective charge of  $2.9 \pm 0.1$  for Pu(VI) and by analogy to Np(V) the effective charge of Pu(V) is assumed to be  $\sim 2.2$ . The effective charge of the plutonium ion greatly affects its environmental behaviour because the aqueous plutonium ions are hard acids and tend to form strong complexes with ligands containing oxygen donor atoms. The strength of the bond between a plutonium cation and ligand is proportional to the effective charge of the plutonium cation. Generally, as the effective charge increases, the ionic bonds that are formed become shorter and stronger. Because Pu(IV) has the highest effective charge of all the plutonium oxidation states, it is assumed that aqueous  $\text{Pu}^{4+}$  will be removed from the aqueous phase via sorption (or precipitation) and is therefore the least mobile form of plutonium in the environment. Conversely, Pu(V) is considered to be the most mobile due to its relatively low effective charge and, therefore, weak complex formation.

Because of ion-dipole interactions, a series of hydration spheres surround plutonium ions in solution. The primary hydration sphere is composed of strong electrostatic interactions between water and the central plutonium ion. Secondary hydration spheres form through hydrogen bonding of water molecules with those in the primary hydration sphere and experience a lower level of electrostatic attraction from the central plutonium ion. Table 1 shows the number of coordinating waters in the primary hydration sphere for each oxidation state of plutonium and the corresponding Pu-O distance. A secondary hydration sphere is formed as a result of dipole-dipole interactions between the waters that make up the primary hydration sphere and bulk water.

Generally, the entropy associated with hydration becomes more positive as the effective charge decreases:  $\text{Pu}^{4+} > \text{Pu}^{3+} >$

Table 1 - Number of coordinating waters and distance of the hydration sphere for each plutonium oxidation state.

Oxidation State	General Formula	Number of Coordinating Waters (n)	Pu-O Distances (Å)
III	$\text{Pu}(\text{OH}_2)_n^{3+}$	9 <sup>36,37</sup>	2.48(1) <sup>36</sup>
		10 <sup>38</sup>	2.51(1) <sup>37,38</sup>
IV	$\text{Pu}(\text{OH}_2)_n^{4+}$	8 <sup>36,39</sup>	2.39(1) <sup>36</sup>
V	$\text{PuO}_2(\text{OH}_2)_n^+$	4–5 <sup>36</sup>	2.47(1) <sup>36</sup>
VI	$\text{PuO}_2(\text{OH}_2)_n^{2+}$	4–5 <sup>36</sup>	2.41(1) <sup>36</sup>

$\text{PuO}_2^{2+} > \text{PuO}_2^+$ .<sup>40</sup> The more negative entropy for Pu(IV) relative to Pu(VI) and Pu(V) favours increased hydration. This is supported by the extended X-ray absorption fine structure (EXAFS) data in Table 1, which shows that  $\text{Pu}^{4+}$  has 8 coordinating waters in its primary hydration sphere whereas  $\text{PuO}_2^+$  and  $\text{PuO}_2^{2+}$  have 4–5 coordinating waters in their primary hydration spheres. In addition to the hydration sphere surrounding aqueous plutonium species, mineral surfaces are also hydrated. Inner-sphere sorption (or adsorption) of plutonium to a mineral surface requires the displacement of solvating waters from both the plutonium ion and the mineral surface.

The chemical thermodynamics of a system describe the overall energy changes that occur when transitioning from one state to another and are described by the standard-state free energy of reaction ( $\Delta G^\circ$ ). The free energy associated with sorption of plutonium to a mineral surface has two components – the free energy associated with bonding ( $\Delta G^\circ_{\text{chemical}}$ ) and the free energy associated with electrostatic interactions ( $\Delta G^\circ_{\text{electrostatics}}$ ). Electrostatic interactions refer to those between a charged mineral surface and a charged aqueous plutonium ion (or complex). A positively charged surface will repel plutonium cations; a negatively charged surface will attract plutonium cations. However, plutonium sorption to mineral phases is observed even when the pH of the system is below the point of zero charge (PZC) of the mineral surface (i.e., the surface is positively charged). This is due to the free energy associated with deprotonating the surface and the formation of O-Pu bonds with a metal oxide surface. The free energy of bonding is affected by steric constraints such as ion size, the presence of actinyl oxygens, and ligands. Attraction is proportional to the product of effective charges.

### Oxidation-reduction behaviour

As mentioned above, plutonium can be in the +3, +4, +5, and +6 oxidation states; the +2 and +7 oxidation states are also observed under extreme conditions. As seen in Table 2, the potentials for all plutonium couples are around 1.0 V in acidic solution (i.e., 1 M  $\text{HClO}_4$ ). This similarity in redox potentials means that plutonium is very sensitive to even minor changes in the  $E_h$  of the system; changes in oxidation state readily occur. Thus, under acidic conditions, all four oxidation states can exist simultaneously. When the pH of the system is raised, the reduction potential for the Pu(IV)/Pu(III) couple becomes

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Table 2 - Formal electrochemical potentials for redox couples relating the plutonium ions in acidic (1 M HClO<sub>4</sub>), neutral (pH 8), and basic (1 M NaOH) aqueous solutions versus the standard hydrogen electrode. Adapted from Clark et al.<sup>3</sup>

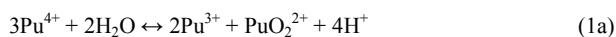
Redox Reaction	Acidic	Neutral	Basic
Pu(III) ↔ Pu(IV) + e <sup>-</sup>	+0.982	-0.39	-0.96
Pu(IV) + 2H <sub>2</sub> O ↔ Pu(V) + 4H <sup>+</sup> + e <sup>-</sup>	+1.170	+0.70	-0.67
Pu(V) ↔ Pu(VI) + e <sup>-</sup>	+0.913	+0.60	+0.12
Pu(IV) + 2H <sub>2</sub> O ↔ Pu(V) + 4H <sup>+</sup> + 2e <sup>-</sup>	+1.043	+0.65	+0.34
Pu(III) + 2H <sub>2</sub> O ↔ Pu(V) + 4H <sup>+</sup> + 2e <sup>-</sup>		+1.076	

negative and it is generally assumed that Pu(III) becomes unstable in solution. While Olsson<sup>41</sup> demonstrated that the trivalent oxidation state cannot be maintained in aqueous systems that are open to the air and have pH > 2, Kaplan et al.<sup>42</sup> found Pu(III) associated with sediments from the Savannah River Site where the pH is between 6 and 7 and the E<sub>h</sub> is between 250 mV and 500 mV, Marsac et al.<sup>43</sup> observed Pu(III) in high saline solutions (< 3.2 m NaCl) when the pH is between 3 and 6 and the pe is between 2 and 10, and Felmy et al.<sup>44</sup> showed that the reduction of PuO<sub>2</sub>(am) by Fe(II) yields aqueous Pu(III) under argon atmosphere. Under circumneutral conditions, the reduction potentials for the Pu(V)/Pu(IV), Pu(VI)/Pu(V), and Pu(VI)/Pu(IV) couples remain similar; therefore, Pu(IV), Pu(V), and Pu(VI) may exist simultaneously at neutral pH. Under alkaline conditions (i.e., 1 M NaOH), the redox potential for the Pu(V)/Pu(IV) couple is also negative. Therefore, higher pH conditions may favour the plutonyl (i.e., Pu(V) and Pu(VI)) species. Under alkaline conditions, the reduction potentials of each redox couple are not as close as they are under acidic and neutral conditions.

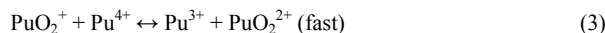
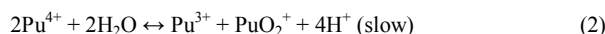
Note that the Pu(III)/Pu(IV) and Pu(V)/Pu(VI) half-reactions are not dependent on the pH of the solution. The double-bonded axial oxygens of Pu(V) and Pu(VI) do not need to be formed or broken for reversible redox reactions to occur. However, the other redox reactions exhibit pH dependence. Structural rearrangement occurs in these reactions in order for axial Pu-O double bonds to form or dissolve.

### Disproportionation

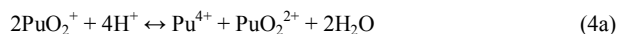
The disproportionation of Pu(IV) and Pu(V) also contributes to the existence of multiple plutonium oxidation states in solution. Connick<sup>45</sup> and Rabideau<sup>46,47</sup> studied these disproportionation reactions at pH < 1 and found that each involves a two-step process that does not rely on the oxidation or reduction of water or other elements as electron shuttles. For the disproportionation of Pu(IV) (reaction 1a), the slow step involves two Pu(IV) ions combining to form Pu(III) and Pu(V) (reaction 2). This reaction is slow because it involves the formation of an axial oxygen double bond in PuO<sub>2</sub><sup>2+</sup>. In the second step (reaction 3), the Pu(V) produced in reaction 2 reacts with a third Pu(IV), yielding Pu(III) and Pu(VI). The disproportionation is complete when both reactions have reached equilibrium.



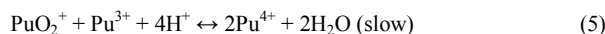
$$K = \frac{\{\text{Pu}^{3+}\}^2\{\text{PuO}_2^{2+}\}\{\text{H}^+\}^4}{\{\text{Pu}^{4+}\}^3\{\text{H}_2\text{O}\}} \quad (1b)$$



The overall disproportionation of Pu(V) at pH < 1 is provided in reaction 4a. The slow step (reaction 5) is the reverse of the slow step for Pu(IV) disproportionation; the fast step is identical for both disproportionation reactions.

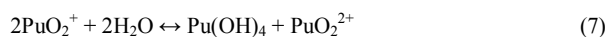
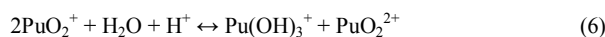


$$K = \frac{\{\text{Pu}^{4+}\}\{\text{PuO}_2^{2+}\}^2\{\text{H}_2\text{O}\}}{\{\text{PuO}_2^{2+}\}^2\{\text{H}^+\}^4} \quad (4b)$$



If there is little or no Pu(III) in solution, Pu(V) disproportionation will proceed via reactions 3 and 4a, where reaction 4a is the rate-determining step and reaction 3 is assumed to reach rapid equilibrium.<sup>47</sup>

Disproportionation is a function of plutonium concentration and pH. The third and second order dependence of disproportionation equilibrium constants on Pu<sup>4+</sup> (reaction 1b) and PuO<sub>2</sub><sup>2+</sup> (reaction 4b) concentration, respectively, indicates that disproportionation will increase as the plutonium concentration of the system increases. Additionally, the equilibrium constant for the disproportionation of Pu(IV), based on equation 1b, has a fourth order dependence on the hydrogen ion concentration. Conversely, the equilibrium constant for the disproportionation of Pu(V), based on equation 4b, has an inverse fourth order dependence on the hydrogen ion concentration in solution. Therefore, according to the reactions above, as the pH of the system is lowered, the disproportionation of Pu(IV) becomes less important while the disproportionation of Pu(V) becomes more important. However, these reactions do not take into consideration the effects of plutonium hydrolysis as the pH of the system is raised. Extrapolation of this effect is difficult. For example, the disproportionation of Pu(V) at circumneutral pH could be described by reaction 6, 7, or 8.<sup>21</sup>



Because each of reaction 6 - 8 exhibits a different pH dependence, it is unclear what influence disproportionation may have across the pH range and further studies in this area are warranted. As an example, Budantseva et al.<sup>48</sup> observed the disproportionation of Pu(V) in strongly alkaline solutions (i.e., 4-8 M NaOH). The products were aqueous Pu(VI) and a Pu(IV) hydrous oxide precipitate. Alpha radiolysis and sorption onto the precipitated Pu(IV) complicated data interpretation.

Furthermore, the above reactions do not take into consideration the formation of the Pu(IV) colloid. Newton et al.<sup>49</sup> observed the formation of the Pu(IV) colloid in solutions where initial conditions were 10 to 34 mM Pu(V) at pH < 2 and suggested that a critical concentration of Pu(IV) colloid is required before significant amounts of disproportionation are observed. This supports the observation made by Madic et al.<sup>50</sup> in which a <sup>242</sup>Pu(V) solution was stable for days at pH < 3.7. Under neutral to alkaline solutions Neck et al.<sup>51</sup> show that small Pu(IV) colloids or polymers play an important role in redox transformations. The transfer of Pu(V/VI) to reduced Pu(III/IV) states proceeds via the formation of these colloids. Thus, reactions 6 – 8 may not be relevant for some environmental investigations.

Despite the mechanistic understanding of Pu(IV) and Pu(V) disproportionation discussed above, based on the work of Connick<sup>45</sup> and Rabideau<sup>46,47</sup> and corroborated by others,<sup>50,52,53</sup> much research still needs to be done. Most studies were performed in strongly acidic solutions (pH < 2) and in matrices not representative of environmental samples. Understanding how plutonium hydrolysis and changes in ionic strength affects the disproportionation mechanisms and kinetics are important future research questions.

### Solubility

Plutonium solubility has been widely studied under a range of experimental conditions. Thorough analyses of these data are provided elsewhere<sup>51,54–57</sup> so the discussion below is limited to an overview of the present state of knowledge. In general, the solubility of plutonium under reducing conditions or in the presence of air at low pH are well defined whereas less is understood about the solubility of plutonium in the presence of oxygen.<sup>51,54,55</sup> Regardless, the low solubilities highlighted below are expected to limit the mobility of plutonium in the subsurface environment.

The solubility of Pu(III) has been largely overlooked with only one peer-reviewed study available in the literature. Felmy et al.<sup>58</sup> determined the solubility for Pu(III) with respect to Pu(OH)<sub>3</sub>(s) in solutions containing iron powder to maintain reducing conditions. The solubility product extrapolated to zero ionic strength (log  $K_{sp}^{\circ}$ ) is  $-26.2 \pm 0.8$ . However, thermodynamic calculations show that Pu(OH)<sub>3</sub>(s) is not stable and should convert to PuO<sub>2</sub>(am,hyd) or PuO<sub>2</sub>(s,hyd), particularly if the redox potential of the system is sufficiently high to promote Pu(III) oxidation to Pu(IV).<sup>51,59</sup> In simulated brines with ionic strengths of ~6 and ~10, the solubility of Pu(III) increases by two to four orders of magnitude, respectively, at pH < 9.<sup>58</sup> The increased solubility in synthetic brine is attributed to Pu<sup>3+</sup>-Cl<sup>-</sup> interactions in the aqueous phase.<sup>58</sup>

Pu(IV) is known to form amorphous hydroxides, denoted Pu(OH)<sub>4</sub>(am), and hydrous oxides, denoted PuO<sub>2</sub>·xH<sub>2</sub>O(s), PuO<sub>2</sub>(s,hyd), or PuO<sub>2</sub>(am,hyd). There are large discrepancies in

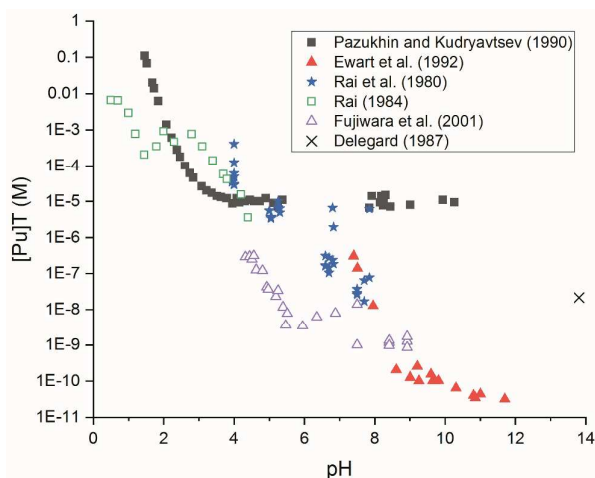
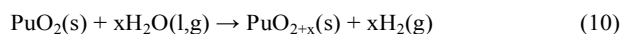


Figure 2 - Solubility of Pu(IV) with respect to Pu(OH)<sub>4</sub>(am) (closed symbols) and PuO<sub>2</sub>·xH<sub>2</sub>O(s) (open symbols). The solid phase in Delegard (1987) (reference 61) is referred to as Pu(IV) hydrous oxide.

the solubility data for Pu(IV) (see Figure 2). For example, reported log  $K_{sp}^{\circ}$  values for Pu(OH)<sub>4</sub>(am) range from  $-59.9 \pm 0.3$  to  $-57.8 \pm 0.3$  with an average of  $-58.5 \pm 0.7$ .<sup>56,60</sup> The large scatter in the data can be partially attributed to the disproportionation of Pu(IV), Pu(IV) colloid formation, and uncertainty in the composition of the solid phase. However, some generalizations can be made. The solubility of Pu(OH)<sub>4</sub>(am) increases with increasing NaOH concentration,<sup>57,61</sup> carbonate concentration,<sup>57,62</sup> and bicarbonate concentration<sup>57,62</sup> but generally decreases with increasing pH.<sup>57,62–67</sup>

One particularly interesting aspect of plutonium solubility is the formation of PuO<sub>2+x</sub>(s). Haschke and coworkers<sup>68–70</sup> suggest that PuO<sub>2+x</sub>(s) not only forms, but is more thermodynamically stable than PuO<sub>2</sub>(s) in air. Experimental studies by Neck et al.<sup>71</sup> confirm that the  $\Delta_r G_m^{\circ}$  for PuO<sub>2+x</sub>(s,hyd) is slightly more negative than that of PuO<sub>2</sub>(s,hyd). Oxygen is scavenged by PuO<sub>2</sub>(am,hyd) to form PuO<sub>2+x</sub>(am,hyd) according to reaction 9<sup>59</sup> or from the reaction of PuO<sub>2</sub>(s) with water according to reaction 10.<sup>68–70</sup> In principle, reactions 9 and 10 are interchangeable, but writing them as separate reactions highlights two potential mechanisms for PuO<sub>2+x</sub> formation.



The exact structure of PuO<sub>2+x</sub> is unknown, but EXAFS and XPS studies have confirmed that it is a mixed-valent oxyhydroxide solid.<sup>72–74</sup> Neck et al.<sup>59</sup> showed that the measured Pu(V) concentrations and pe values above pH 3 could only be explained by the presence of PuO<sub>2+x</sub>(am,hyd) as the solubility-controlling phase in equilibrium with aqueous Pu(IV) and Pu(V).

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## Environmental Sciences: Processes &amp; Impacts

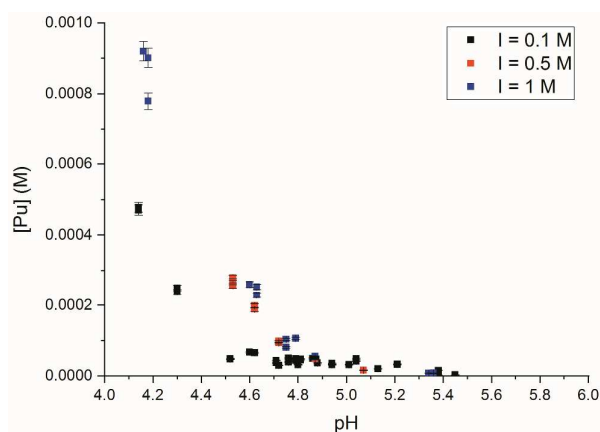
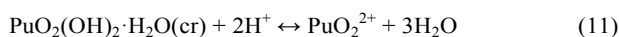


Figure 3 - Solubility of Pu(VI) as a function of ionic strength. Data from reference 75.

The solubility of Pu(V) has not been reported in the peer-reviewed literature and is generally not well understood due to the propensity of Pu(V) to disproportionate and participate in other redox reactions. For example, Budantseva et al.<sup>48</sup> reported that Pu(V) disproportionates to a Pu(IV) hydrous oxide precipitate and dissolved Pu(VI) under alkaline conditions.

In carbonate-free solutions, Pu(VI) is in equilibrium with  $\text{PuO}_3 \cdot x\text{H}_2\text{O}(\text{s})$  (also sometimes denoted as  $\text{PuO}_2(\text{OH})_2 \cdot \text{H}_2\text{O}(\text{s})$ ) across the entire pH range.<sup>57,75</sup> The solubility curve is shown in Figure 3. Reported  $\log K_{\text{sp}}^{\circ}$  values for Pu(VI) hydrous oxide range from  $-24.65 \pm 0.26$  to  $-21.10$  and decrease slightly as the ionic strength of the solution is increased from 0.1 to 1 M  $\text{NaClO}_4$ .<sup>75</sup> In the presence of carbonate, the dominant solid phase is  $\text{PuO}_2\text{CO}_3(\text{s})$ <sup>76-78</sup> with a  $\log K_{\text{sp}}^{\circ}$  value of  $-14.82 \pm 0.05$ .<sup>78</sup> However, Pashalidis et al.<sup>76</sup> show that  $\text{PuO}_2\text{CO}_3(\text{s})$  transforms into  $\text{PuO}_2(\text{OH})_2(\text{s})$  in the absence of carbon dioxide. The Nuclear Energy Agency Thermochemical Database project (NEA-TDB) uses  $\log^* K_{\text{sp}} = 5.5 \pm 1.0$  for reaction 11.<sup>54,55</sup>



Several studies have been conducted investigating the solubility of plutonium in environmental systems. Efurud et al.<sup>67</sup> studied the solubility of plutonium in J-13 well water, which is a reference water for the unsaturated zone near the proposed Yucca Mountain repository in the United States. It is a low ionic strength groundwater dominated by hydroxide and carbonate. At pH 6 and 25°C, the solubility of plutonium is  $(4.70 \pm 1.13) \times 10^{-8}$  M.<sup>67</sup> There is a slight decrease in plutonium solubility with increasing pH at 25°C – less than an order of magnitude over the pH range 6 to 8.5 – and the solubility-limiting solid is an unknown, poorly crystalline Pu(IV) phase. Similar, earlier studies by Nitsche et al.<sup>79</sup> as a function of initial plutonium oxidation state reported aqueous plutonium concentrations ranging from  $3.0 \times 10^{-8}$  –  $7.6 \times 10^{-7}$  M; Pu(VI) was the predominant oxidation state in the aqueous phase. The solubility-limiting phase in solutions where plutonium is

added as Pu(III) or Pu(IV) is an unidentified crystalline phase whereas  $\text{NaPuO}_2\text{CO}_3(\text{s})$  is the solubility-limiting phase in solutions where plutonium is added as Pu(V) or Pu(VI).

### Colloid Formation

Under elevated plutonium concentrations, Pu(IV) is known to hydrolyse and form an intrinsic plutonium oxide colloid (also referred to as  $\text{PuO}_{2+x}(\text{s})$  or Pu polymer).<sup>33,34,71,80</sup> It is important to make the distinction between intrinsic (or eigen-) plutonium colloids and plutonium pseudo-colloids. Intrinsic colloids are formed through hydrolysis of plutonium to form an oxide phase whereas pseudo-colloids are inorganic or organic colloids which plutonium may sorb to.<sup>33</sup> In either case, the small size of these particles ( $< 1 \mu\text{m}$ ) allows them to move with water through pore spaces, thereby enhancing Pu(IV) mobility in the subsurface environment.

Transport models and their supporting sorption models have been unable to predict the enhanced mobility of plutonium at several field sites. Santschi et al.<sup>81</sup> showed that the natural organic matter present in soils at the Rocky Flats Environmental Technology Site stabilised colloidal plutonium, leading to elevated levels of plutonium in storm runoff. Most of the plutonium was found in the particulate ( $> 0.5 \mu\text{m}$ ) and colloidal ( $> 3 \text{kDa}$ ) phases, as opposed to the dissolved phase. In addition, plutonium in the colloidal fraction was preferentially associated with organic macromolecules as opposed to iron (oxyhydr)oxide or clay colloids. Furthermore, the kilometre-scale transport of plutonium at the former Nevada Test Site and Mortendad Canyon (LANL) is attributed to plutonium pseudo-colloid formation<sup>82,83</sup> whereas kilometre-scale transport of plutonium at the Mayak Production Association is attributed to both intrinsic and pseudo-colloids.<sup>84</sup> These findings demonstrate the weaknesses of current empirical sorption and transport models, which are unable to predict the speciation of plutonium in aqueous and solid phases, particularly with regard to colloidal species.

Despite the recognized importance of colloid-facilitated transport, little is known about the geochemical mechanisms controlling plutonium colloid formation and association. The extent and mechanism(s) of colloid-facilitated transport, in turn, require a firm understanding of intrinsic plutonium colloid formation, structure, and stability. The current state of knowledge has been recently summarized by Kersting et al.<sup>33</sup> Walther and Denecke,<sup>85</sup> and Zänker and Hennig.<sup>34</sup> The reader is referred to these documents for a thorough review of colloid-facilitated Pu(IV) transport.

### Ligand Interactions

In natural fresh waters, common inorganic ligands include hydroxide, carbonate, phosphate, fluoride, chloride, and sulphate. Because of the relatively high concentration of hydroxide and carbonate in natural waters,<sup>86</sup> the discussion below will focus on the effect of hydrolysis and carbonate complexation have on plutonium aqueous chemistry. Common

organic ligands include natural organic matter (NOM), such as humic and fulvic acids. Although organic ligands are important in environmental systems because of their complexation and redox properties,<sup>87</sup> a detailed description of their influence on plutonium aqueous chemistry is outside the scope of this review, which is limited to a discussion of binary plutonium-mineral systems.

All plutonium species readily undergo hydrolysis, which occurs when the positive charge on the plutonium ion polarizes water sufficiently to remove a proton. While hydrolysis is important across the entire pH range for the +3, +4, and +6 oxidation states of plutonium, Pu(V) does not hydrolyse until alkaline conditions exist (see Electronic Supplementary Information (ESI)). Pu(IV) is successively hydrolysed to  $\text{Pu}(\text{OH})_2^{2+}$ ,  $\text{Pu}(\text{OH})_3^+$ , and  $\text{Pu}(\text{OH})_4(\text{aq})$  while Pu(V) remains as the free dioxo cation until it is hydrolysed at approximately pH 10.

As discussed above, the tendency of plutonium to undergo hydrolysis decreases as the effective charge of the ion increases following the trend  $\text{Pu}^{4+} > \text{PuO}_2^{2+} \approx \text{Pu}^{3+} > \text{PuO}_2^+$ . Therefore, hydrolysis is the most evident for  $\text{Pu}^{4+}$  and the least prominent for  $\text{PuO}_2^+$ . This is supported by the observation that Pu(V) exists as the free cation over part of the pH range while Pu(IV) does not (see ESI).

Carbonate is present in aqueous solutions that are in contact with carbonate minerals or through the dissolution of carbon dioxide in water forming carbonic acid. Subsequent deprotonation of carbonic acid creates bicarbonate and carbonate in solution. Based on published  $\text{pK}_a^\circ$  values,<sup>86</sup> interaction of plutonium with bicarbonate and carbonate need to be taken into consideration at pHs above 6.3 and 10.3, respectively. The effect of carbonate concentration on Pu(IV) and Pu(V) aqueous speciation is shown in the ESI. In solutions containing  $10^{-8}$  M Pu(IV) and 0.1 M carbonate, plutonium carbonate species dominate across the pH range until approximately pH 12, when  $\text{Pu}(\text{OH})_4(\text{aq})$  is the dominant aqueous species. Under the same conditions,  $\text{PuO}_2^+$  is the dominant species below pH  $\sim 6$ , which yields to plutonium carbonate species at higher pH values. These modelling results are not surprising given the high  $\log \beta_{1,i}^\circ$  values presented in the ESI. As a comparison, the  $\log \beta_{1,i}^\circ$  values for Pu(IV) hydrolysis and Pu(IV) carbonate complexation are shown in Figure 4. The  $\log \beta_{1,i}^\circ$  values were taken from Clark et al.<sup>3</sup> and adjusted for the  $\log K_w$  of water using equation 12

$$\log \beta_{1,i}^\circ = \log \beta_{1,i}^\circ - n \log K_w \quad (12)$$

where  $n$  is the number of waters involved in the hydrolysis reaction. The  $\log \beta_{1,i}^\circ$  values were taken from Clark et al.<sup>88</sup> and adjusted to zero ionic strength using the Davies equation. This favourability towards Pu-carbonate complexation may have a profound impact on plutonium sorption if the Pu-carbonate complexes that are formed have a negative charge. If the pH of solution is above the PZC, then the electrostatic repulsion between the negatively-charged mineral surface and

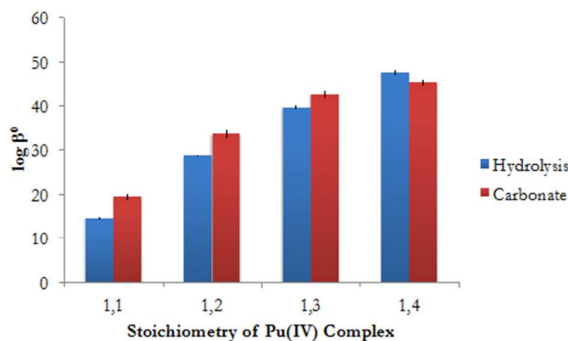


Figure 4 - Cumulative formation constants for the hydrolysis and carbonate complexation of Pu(IV). Values for Pu(IV) hydrolysis and Pu(IV)-carbonate adapted from references 3 and 88, respectively.

negatively-charged plutonium carbonate species would lead to a  $\Delta G^\circ_{\text{electrostatics}}$  that is not favourable.

### Plutonium speciation in natural waters

Figure 5 is a generalized Pourbaix diagram that shows the dominant aqueous plutonium species that exist in a solution that is equilibrated with carbon dioxide.<sup>55</sup> In the stability field of most natural waters (-0.2 to +0.6 V and pH 4-9), Pu(III), Pu(IV), and Pu(V) are the dominant aqueous-phase oxidation states;  $\text{PuO}_2(\text{s})$  and  $\text{Pu}(\text{OH})_4(\text{s})$  are the stable solid phases but have been excluded from the simulation.<sup>89</sup> For example, the pH and  $E_H$  of J-13 well water were determined to be 7.4 and 0.43 V, respectively.<sup>67</sup> Under these conditions, the predominant plutonium species in J-13 well water is  $\text{Pu}(\text{OH})_4(\text{aq})$ ;  $\text{PuO}_2^+$  and  $\text{PuO}_2\text{CO}_3^-$  may also be important species.<sup>89</sup> Pu(III) is stable at low redox potentials and the stability field of Pu(VI) species is relatively small. Addition of anions such as chloride and sulphate yield some Pu(VI)-chloride and sulphate complexes at low pH. However, relatively high concentrations (i.e., > 0.5 M chloride and > 0.02 M sulphate) similar to the values found in seawater) are required.<sup>86</sup>

Nelson and Lovett<sup>90</sup> measured the concentration of Pu(IV) and Pu(VI) in the Irish Sea near the Windscale reprocessing plant, which was authorized to release 1 pCi L<sup>-1</sup> plutonium at a distance of 2.4 km from the shoreline. The results are summarized in Table 3. The particle size refers to concentrations of plutonium without filtration, after filtration through a 0.22  $\mu\text{m}$  filter, or after filtration through both the 0.22  $\mu\text{m}$  filter and a 0.025  $\mu\text{m}$  filter. Plutonium rejected by the filters is predominantly Pu(IV). Nelson and Lovett<sup>90</sup> assumed that any oxidized plutonium was present as Pu(VI), but other studies provide evidence that the oxidized form of plutonium in natural waters is Pu(V).<sup>26,27,91</sup> When dissolved organic matter is present, Pu(V) or Pu(VI) could be the dominant form of plutonium depending on the  $E_H$  of the solution.<sup>92</sup> However, the redox reactions between Pu(VI) and natural organic matter should shift the distribution to favour Pu(V).



## ARTICLE

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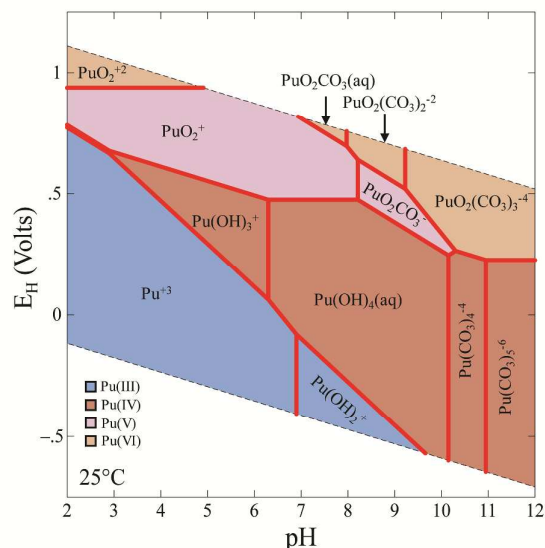


Figure 5 – Pourbaix diagram of plutonium calculated for a solution in equilibrium with  $10^{-3.4}$  bar of  $\text{CO}_2$  at  $25^\circ\text{C}$ . Thermodynamic data from reference 55.

Table 3 - Concentration of Pu(IV) and Pu(VI) in the Irish Sea near the Windscale reprocessing plant. Shoreline samples were collected at a water depth of  $\sim 0.5$  m, surface samples were collected offshore within 1 m of the surface, and bottom samples were collected offshore within 1 m of the seabed. Data from reference 90..

Sample Location	Particle Size ( $\mu\text{m}$ )	Pu(IV) ( $\text{fCi L}^{-1}$ )	Pu(VI) ( $\text{fCi L}^{-1}$ )
Shoreline	$> 0.22$	$11525 \pm 1229$	$423 \pm 247$
	$< 0.22$	$126 \pm 42$	$679 \pm 74$
Surface	$> 0.22$	$231 \pm 22$	$2 \pm 48$
	$0.025 - 0.22$	$28 \pm 10$	$23 \pm 29$
Bottom	$< 0.025$	$45 \pm 5$	$361 \pm 21$
	$> 0.22$	$1250 \pm 52$	$28 \pm 17$
	$0.025 - 0.22$	$-1 \pm 6$	$-10 \pm 8$
	$< 0.025$	$83 \pm 4$	$200 \pm 6$

In natural waters containing high concentrations of carbonate, plutonium is present in the aqueous phase as Pu(IV). In water from Mono Lake, California – a naturally alkaline, saline lake with carbonate concentrations three orders of magnitude higher than seawater – the dissolved concentration of  $^{239,240}\text{Pu(IV)}$  was  $0.01 \text{ pCi L}^{-1}$ .<sup>93–95</sup> This is higher than other natural waters, presumably due to the formation of aqueous carbonate complexes.

### Surface-mediated redox reactions

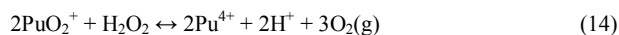
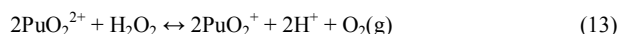
As discussed below, numerous studies have observed the capacity of pure minerals and native soils to reduce or oxidize plutonium. In some studies, the reduction of plutonium is measured directly through the use of spectroscopic techniques, such as X-ray absorption near edge structure (XANES) spectroscopy, whereas in other studies indirect methods, such as solvent extraction, are used. In all cases in which the aqueous-phase oxidation state is measured, no

Pu(IV) is present. Thus, reduction occurs at or near the mineral surface and not in the bulk aqueous phase. Despite these studies, the exact mechanism(s) responsible for surface-mediated redox reactions remain unclear. Hypotheses include: (1) radiolysis at the mineral surface, (2) electron transfer via trace ferrous iron or Mn(II) at the mineral surface, (3) electron shuttling due to the semiconductor properties of the mineral, (4) disproportionation of Pu(V) at the mineral-water interface, (5) stabilisation of Pu(IV) at the mineral surface due to increased concentration gradient within the electrical double layer (EDL), (6) facilitation by proton exchange sites, and (7) reduction based on a Nernstian favourability (i.e., in this work we use the term "Nernstian favourability" to indicate a shift in the reduction potential of the Pu(V)/Pu(IV) surface complex based on formation of Pu(IV) complexes with aqueous species or surface sorption sites which may sufficiently alter the Pu(V)/Pu(IV) reduction potential to allow water to serve as the reductant) of Pu(IV) surface complexes or nanocolloids. The conceptual models supporting these hypotheses are discussed below along with evidence from the literature that supports or disproves each hypothesis.

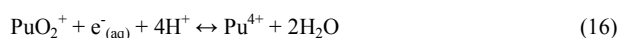
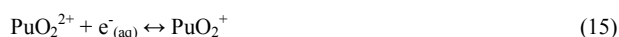
### Proposed mechanisms

**Radiolysis at the mineral surface.** The conceptual model supporting radiolysis at the mineral surface is that alpha particles released from the radioactive decay of plutonium will induce hydrogen peroxide and free radical formation through the splitting of water. These radiolysis products can then react with plutonium, reducing Pu(V) to Pu(IV) either on the mineral surface or in solution, followed by sorption of Pu(IV) to the mineral surface.

Alpha radiolysis of water may produce the following species:  $\text{OH}^\cdot$ ,  $\text{H}^\cdot$ ,  $\text{HO}_2^\cdot$ ,  $\text{e}^-_{(\text{aq})}$ ,  $\text{H}_2$ , and  $\text{H}_2\text{O}_2$ .<sup>96,97</sup> Yields of free-radical products are the highest in solutions irradiated with gamma- and X-rays whereas the molecular products are favoured in solutions irradiated with alpha particles.<sup>96</sup> In plutonium solutions,  $\text{H}_2$  and  $\text{H}_2\text{O}_2$  are expected to be the most relevant alpha radiolysis products.  $\text{H}_2$  will not reduce plutonium in the absence of a catalyst,<sup>96</sup> but hydrogen peroxide can react with plutonium according to reactions 13 and 14, wherein Pu(VI) is reduced to Pu(V) and Pu(V) is reduced to Pu(IV).<sup>98</sup>



Solvated electrons may interact with plutonium according to reactions 15 and 16, analogous to the reaction of Np(VI) and Np(V) with  $\text{e}^-_{(\text{aq})}$ .<sup>99</sup>



G-values can be used to determine the number of hydrated electrons or hydrogen peroxide molecules that will be generated for every 100 eV of energy deposited by an alpha

particle. Therefore, the G-value is dependent upon the plutonium isotope and concentration since the alpha particle energy is slightly different for each plutonium isotope (e.g.,  $^{238}\text{Pu}$  decays via emission of a 5.4992 MeV alpha particle whereas  $^{239}\text{Pu}$  decays via emission of a 5.156 MeV alpha particle). The decomposition of hydrated electrons and hydrogen peroxide in solution must also be taken into consideration and must be slow enough to allow interaction between plutonium and the radiolysis product. Bronskill et al.<sup>100</sup> reported decomposition rate constants of  $10^{13} \text{ days}^{-1}$  for solvated electrons and  $10^{-2} \text{ days}^{-1}$  for hydrogen peroxide.

In one of the first observations of the surface-mediated reduction of Pu(V), Sanchez et al.<sup>13</sup> acknowledged the possibility of reduction via radiolysis but suggested that the concentrations of the radiolysis products would be below detection limits due to the low concentration of  $^{238}\text{Pu}$  used in the studies (i.e.,  $< 1 \times 10^{-10} \text{ M}$ ). Romanchuk et al.<sup>19</sup> also included self-reduction as a potential mechanism for plutonium reduction on hematite ( $\alpha\text{-Fe}^{\text{III}}_2\text{O}_3$ ) but eliminated it from consideration because the plutonium isotope they were using,  $^{237}\text{Pu}$ , decays via electron capture.

Hixon et al.<sup>21</sup> tested whether radiolysis at the mineral surface was a plausible mechanism for the surface-mediated reduction of plutonium in the presence of high-purity quartz ( $\text{SiO}_2$ ). Increasing the total alpha radioactivity of the solution by varying the ratio of  $^{242}\text{Pu}$  to  $^{238}\text{Pu}$  in solution had a negligible effect on the rate of plutonium sorption. Conservative calculations showed that no  $e^-_{(\text{aq})}$  was present in solution due to its rapid decomposition rate and that the greatest amount of hydrogen peroxide in the system was four times less than the amount of plutonium in solution. This research, along with that of Romanchuk et al.,<sup>19</sup> lead to the conclusion that radiolysis at the mineral surface is not a primary mechanism for the surface-mediated reduction of plutonium.

#### Electron transfer via ferrous iron or Mn(II) at the mineral surface.

Iron is ubiquitous in the subsurface environment as iron minerals, which exist in oxidized (e.g., hematite, goethite ( $\alpha\text{-Fe}^{\text{III}}\text{OOH}$ )), mixed valence (e.g., magnetite ( $\text{Fe}^{\text{II}}(\text{Fe}^{\text{III}})_2\text{O}_4$ )), and reduced (e.g., pyrite ( $\text{Fe}^{\text{II}}\text{S}_2$ ), siderite ( $\text{Fe}^{\text{II}}\text{CO}_3$ )) forms, and as a trace constituent of other mineral phases, such as smectite clays. Additionally, repository designs strategically introduce high amounts of reduced iron (e.g., container and emplacement materials) that typically have a pronounced effect on *in-situ* post-closure redox chemistry.<sup>101,102</sup> These iron phases are important not only for the subsurface transport of actinides, where iron minerals are almost always present, but are also an integral part of defining the radionuclide source term for a variety of repository concepts.

Though less abundant than iron, manganese is also prevalent in the environment. Important minerals include pyrolusite ( $\text{Mn}^{\text{IV}}\text{O}_2$  but sometimes reported as  $\beta\text{-MnO}_2$ ), manganite ( $\text{Mn}^{\text{III}}\text{OOH}$ ), cryptomelane ( $\text{K}(\text{Mn}^{\text{IV}}_7\text{Mn}^{\text{III}})\text{O}_{16}$ ), and hausmannite

( $\text{Mn}^{\text{II}}(\text{Mn}^{\text{III}})_2\text{O}_4$ ). Mn(II) is very soluble and can be present in solution through the dissolution of Mn(II)-bearing solid phases or the disproportionation of Mn(III). Mn(II) may interact directly with Pu(V/VI) in the aqueous phase or form an alteration layer at the mineral surface, thereby facilitating electron transfer at the mineral-water interface.

While previous studies have shown that aqueous Fe(II) and Fe(III) facilitate redox cycling of plutonium,<sup>15</sup> the focus of this section is how ferrous iron or Mn(II) at the mineral surface may facilitate surface-mediated redox reactions via electron transfer. In order for electron transfer to occur, plutonium must sorb directly to a Fe(II)- or Mn(II)-bearing surface site.

$^{57}\text{Fe}$  Mössbauer spectroscopy has been used to show that electron transfer occurs between sorbed Fe(II) and structural Fe(III) in hematite,<sup>103</sup> goethite,<sup>104</sup> and the smectite clay nontronite ( $\text{Fe}^{\text{III}}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$  as NAU-2 from the Source Clays Repository (SCR)).<sup>105</sup> At room temperature, the electron transfer rate in nontronite is too fast to be measured experimentally (i.e., faster than  $10^7 \text{ s}^{-1}$ ), but slower than the rates determined for hematite ( $3.6 \times 10^{12} \text{ s}^{-1}$ )<sup>106</sup> and magnetite ( $10^{10} - 10^{12} \text{ s}^{-1}$ )<sup>107</sup> using *ab initio* calculations. Density functional theory (DFT) calculations agree well with these electron transfer rates and suggest that electron transfer occurs mainly within the octahedral sheet on nontronite<sup>108</sup> whereas electron transfer from sorbed Fe(II) to bulk Fe(III) in hematite is facilitated by simultaneous proton transfer between the Fe(II) hydrolysis sphere and surface oxygen species.<sup>109</sup> Iron sorption studies as a function of Fe(II) concentration indicate that up to 15% of the structural Fe(III) is reduced by nontronite at pH 7.5.<sup>105</sup> Powder X-ray diffraction (pXRD) and transmission electron microscopy (TEM) show that sorbed Fe(II) oxidizes to Fe(III) and forms lepidocrocite ( $\gamma\text{-Fe}^{\text{III}}\text{OOH}$ ) when the aqueous-phase Fe(II) concentration is 3 mM.<sup>105</sup> A Fe(III) layer also forms on the surface of hematite.<sup>103</sup>

Sanchez et al.<sup>13</sup> was the first to propose that trace amounts of Fe(II) present at the goethite surface may be responsible for the surface-mediated reduction of Pu(V). This hypothesis is included in other papers<sup>110-113</sup> as a potential mechanism for the surface-mediated reduction of plutonium, but was not directly studied until the 21<sup>st</sup> century when Hixon et al.<sup>18</sup> observed a decrease in the rate of Pu(V) reduction on Savannah River Site sediments as the amount of Fe(II) in the sediments decreased. This experimental result was obtained from vadose zone sediments that had been treated with dithionite-citrate-bicarbonate to selectively leach or reduce iron(III) oxides and phyllosilicate clay minerals. The redox activity of iron-bearing smectite clays (e.g., Na-montmorillonite, ferruginous smectite, and nontronite) is redox-active over a larger  $E_h$  range than would be expected based on the Nernst equation (i.e., 0.5 – 0.8 V versus the 0.24 V expected for the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  redox couple).<sup>114</sup> Thus, trace ferrous iron in native iron(III) oxides and redox-active Fe(III) in phyllosilicate clay minerals could have been the source of the reductant in Savannah River Site sediments.

There are several examples in the literature showing that the mere presence of Fe(II) does not completely account for observed plutonium sorption behaviour. When the initial Pu(V) aqueous-phase concentration is less than  $10^{-7}$  M, sorption is the rate-limiting step and reduction can be attributed to trace amounts of Fe(II) in the iron(III) (oxyhydr)oxide structure.<sup>15,16,23</sup> For example, only 0.12% of the iron in hematite would need to be Fe(II) in order for this mechanism to be plausible in systems studied by Hixon and Powell<sup>23</sup>; only  $4 \times 10^{-5}$  % (wt.) of Fe(II) is needed under the conditions studied by Romanchuk et al.<sup>19</sup> At higher Pu(V) concentrations, surface-mediated reduction is the rate-limiting step and there is insufficient Fe(II) to reduce all of the plutonium.<sup>23</sup> Emerson and Powell<sup>25</sup> used attenuated total reflectance Fourier transform infrared (ATR-FT-IR) spectroscopy to study the surface-mediated reduction of Pu(VI) to Pu(IV) on hematite nanoparticles under high surface loadings (i.e., 22 - 200 mg Pu per gram of hematite). The use of nanoparticles increases the surface area of hematite available to Pu(VI) and also effectively increases the ratio of surface sites to Fe(II) (i.e., more Fe(II) is available at the surface of hematite nanoparticles than bulk hematite). The peak intensity at  $915 - 917 \text{ cm}^{-1}$ , which corresponds to the asymmetric axial oxygen stretch of Pu(VI), decreases with time due to the reduction of Pu(VI) to Pu(IV); Pu(IV) species do not have axial oxygens and therefore will not exhibit the asymmetric axial oxygen stretch. Pseudo-first order Pu(VI) reduction rates calculated from these data collected at high plutonium surface concentrations were approximately ten times slower than reduction rates calculated in other studies performed at lower total plutonium concentrations. In studies with lower plutonium concentrations, trace Fe(II) in the mineral may facilitate more rapid reduction. However, at higher total plutonium concentrations, the Fe(II) concentration is not sufficient (i.e., Pu:Fe molar ratio  $\gg 1$ ) to enhance the reduction rate.

Under anoxic conditions, some Fe(II) minerals can facilitate two-electron reduction of Pu(V). X-ray absorption spectroscopy (XAS) measurements indicate that plutonium is sorbed to magnetite as Pu(III) whereas in solutions containing mackinawite ( $\text{Fe}^{\text{II}}\text{S}$ ), Pu(V) is reduced to Pu(IV), which precipitates on the mineral surface as  $\text{PuO}_2$ .<sup>115</sup> This incomplete reduction of plutonium in contrast with magnetite may be due to the sulphur-terminated faces of mackinawite, which are not thermodynamically favoured for plutonium sorption. Furthermore, performing experiments under strictly anoxic conditions was key to the formation of Pu(III). Magnetite surfaces rapidly oxidize to maghemite under oxic conditions. The pure magnetite surface allowed for formation of a very specific tridentate surface complex on the magnetite (111) surface.<sup>115</sup> Reduction of Pu(V) to Pu(III) and  $\text{PuO}_2$  precipitation are also observed in the presence of chukanovite ( $\text{Fe}^{\text{II}}(\text{CO}_3)(\text{OH})_2$ ). Therefore, although Fe(II) is present in all three of these mineral systems, formation of Pu(III) requires very specific surface sites. Otherwise, Pu(IV) appears to be the

dominant surface species, similar to interactions with other metal oxide minerals.

Both oxidation<sup>17,28,116,117</sup> and reduction<sup>14,17</sup> of plutonium is observed on manganese oxide minerals. Shaughnessy et al.<sup>14</sup> studied the sorption of Pu(VI) onto manganite and hausmannite. In general, sorption increases over the pH range 3 - 8 followed by a decrease in sorption from pH 8 - 10. Especially at pH < 8, sorption to hausmannite is greater than that for manganite. Shaughnessy et al.<sup>14</sup> attribute this difference in plutonium behaviour to a higher surface site density on hausmannite than manganite. However, this behaviour may be due to preferential binding sites on hausmannite versus manganite. Since manganite is a Mn(III) mineral and hausmannite is a mixed Mn(II/III) mineral, increased sorption on hausmannite relative to manganite may be due to the Mn(II) sites present in hausmannite. More efficient reduction of Pu(VI) via oxidation of Mn(II) to Mn(IV) may also increase sorption to hausmannite due to the higher affinity of Pu(IV) for mineral surfaces.

From X-ray absorption near edge structure (XANES) measurements, Shaughnessy et al.<sup>14</sup> determined that a mixture of Pu(IV) and Pu(V) is associated with both manganese minerals regardless of pH (pH range 5 - 10) when plutonium is added as Pu(VI). It is unclear whether Pu(V) is associated with the mineral surfaces or whether its contribution to the XANES spectrum is the result of interstitial water since the samples were measured as wet pastes. Optical absorption spectra show the presence of Pu(V) in solution within 24 hours, but no Pu(IV) is observed. This indicates that Pu(VI) is reduced to Pu(V) in solution, which then undergoes surface-mediated reduction to Pu(IV). Pu(V) is not reduced to Pu(IV) in solution and Pu(VI) reduction to Pu(V) only occurs in the presence of manganite or hausmannite (i.e., in controls containing no mineral, no plutonium reduction was observed<sup>14</sup>).

Morgenstern and Choppin<sup>117</sup> studied Pu(IV) sorption in the presence of birnessite ( $\text{Na}_{0.5}(\text{Mn}^{\text{III}}, \text{Mn}^{\text{IV}})_2\text{O}_4 \cdot 1.5\text{H}_2\text{O}$ , sometimes reported as  $\delta\text{-MnO}_2$ ) at low pH (i.e., 2.0 - 3.5). A decrease in the fraction of Pu(IV) correlates with an increase in the fraction of Pu(V) and Pu(VI) in the total system (aqueous and solid phases). After five days, the oxidation state distribution is approximately 60% Pu(V) and 40% Pu(IV/VI). This provides circumstantial evidence of surface-mediated oxidation of Pu(IV). This behaviour may be preferential at low pH where the oxidized Pu(V) and Pu(VI) will partition to the aqueous phase rather than remain associated with the solid phase.

The oxidation state distribution of plutonium in the presence of birnessite at pH 8 is very different where the rate of oxidation at pH 8 was hindered and plateaued near 20% of the total plutonium becoming oxidized.<sup>117</sup> Although there is still a decrease in the fraction of Pu(IV) in the system that is accompanied by an increase in the fraction of Pu(V) and Pu(VI), Pu(IV) remains the dominant oxidation state. Solutions containing no birnessite did not indicate significant oxidation

of plutonium. Morgenstern and Choppin<sup>117</sup> attribute the difference in oxidation state distribution between acidic and neutral conditions to the formation of the neutral Pu(OH)<sub>4</sub> aqueous hydrolysis product at neutral pH and hypothesize that surface-mediated oxidation is more thermodynamically favoured under acidic than neutral conditions. This preferential formation of Pu(IV) on MnO<sub>2</sub> surfaces is further demonstrated at longer equilibration times where Pu(IV) remained the dominant oxidation state on pyrolusite (another MnO<sub>2</sub> mineral) at higher pH values.<sup>17</sup> Similar to studies with birnessite, oxidation and partitioning of Pu(V) and Pu(VI) to the aqueous phase occurred at low pH values.

Powell et al.<sup>17</sup> show why both oxidation and reduction of plutonium is observed on manganese oxide minerals. At pH 2.6, approximately 60% of plutonium added as Pu(IV) is initially sorbed to pyrolusite. However, with increasing equilibration time, the amount of plutonium associated with the solid phase decreases. The oxidation state of the total system indicates a decrease in Pu(IV) with a corresponding increase in Pu(V/VI). No Pu(IV) is detected in the aqueous phase. This indicates that plutonium initially sorbs to pyrolusite as Pu(IV) and undergoes subsequent surface-mediated oxidation to Pu(V/VI), which partitions back into the aqueous phase. Plutonium behaves differently at pH 8.2. Within 5 minutes of adding Pu(IV) to a solution containing pyrolusite, approximately 20% of the plutonium in the total system is Pu(V/VI). This corresponds to a slight decrease in plutonium sorption. However, with time, Pu(V/VI) repartitions to the surface and is reduced to Pu(IV) leading to an increase in plutonium sorption. This indicates that, given enough time, plutonium associated with the pyrolusite surface and aqueous phase will be Pu(IV) and Pu(V/VI), respectively.

**Electron shuttling due to the semiconducting properties of the mineral.** Iron (oxyhydr)oxides and manganese oxide minerals are semi-conductors, meaning that the valence electrons in these minerals are free to move between atoms in the crystal's conduction band. The ease with which electrons from the valence band are promoted to the conduction band is based on the energy of the band gap separating the valence and conduction bands.<sup>118</sup> Table 4 provides the band gaps for common iron (oxyhydr)oxide and manganese oxide minerals. Based on these values, exposure to sunlight (3.1 eV) may be sufficient to promote electrons from the valence band to the conduction band. Thus, Pu(V) does not have to sorb directly onto an Fe(II)- or Mn(II)-bearing site since electrons can be shuttled through the bulk mineral. This mechanism is supported by an observed increase in the rate of Pu(V) sorption to goethite and hematite with increasing light intensity<sup>16,19,28</sup> as well as an increase in the sorption of Pu(V) to marine sediments with decreasing wavelength of light irradiation.<sup>119</sup>

A second mechanism supporting the hypothesis that plutonium surface-mediated reduction is due to the

semiconducting nature of the mineral is that photochemically-induced dissolution of Fe(II)/Mn(II) from the mineral structure into the aqueous phase may occur<sup>120</sup> followed by slow oxidation to Fe(III)/Mn(III), such that both oxidation states may be present in the aqueous phase. This leads to the possibility of simultaneous oxidation of Pu(V) to Pu(VI) by Fe(III)/Mn(III) and reduction of Pu(V) to Pu(IV) by Fe(II)/Mn(II) and may also explain the oxidation of plutonium on manganese minerals observed by several researchers,<sup>17,117</sup> which was discussed above. Divalent iron may also be present in the aqueous phase as a result of the reductive dissolution of iron oxide minerals.<sup>121</sup>

Table 4 – Band gaps for several iron (oxyhydr)oxide and manganese oxide minerals.

Mineral	Band Gap (eV)	Reference
Hematite ( $\alpha$ -Fe <sub>2</sub> O <sub>3</sub> )	2.2	Romanchuk et al. <sup>19</sup>
	2.34	Waite <sup>122</sup>
Goethite ( $\alpha$ -FeOOH)	2.5	Sherman <sup>120</sup>
Magnetite (Fe <sub>3</sub> O <sub>4</sub> )	0.1	Kirsch et al. <sup>115</sup>
$\beta$ -MnO <sub>2</sub>	0.26	Waite <sup>122</sup>
Pyrolusite (MnO <sub>2</sub> )	1	Sherman <sup>120</sup>
Cryptomelane (KMn <sub>8</sub> O <sub>16</sub> )	1.2	Sherman <sup>120</sup>
Na Birnessite (Na <sub>0.5</sub> Mn <sub>2</sub> O <sub>4</sub> ·1.5H <sub>2</sub> O)	1.8	Sherman <sup>120</sup>

Kirsch et al.<sup>115</sup> investigated Pu(V) sorption and reduction on three Fe(II)-bearing minerals. Magnetite is a semiconductor, mackinawite is a metallic conductor, and chukanovite has no known (semi)conducting properties. The complete reduction of Pu(V) to Pu(III) in the presence of magnetite is perhaps expected. Similar reduction behaviour would be expected for mackinawite when in fact partial reduction of Pu(V) to PuO<sub>2</sub> is observed. Finally, if electron shuttling were the only mechanism for the surface-mediated reduction of plutonium, we would expect no reduction; instead, reduction of Pu(V) to both PuO<sub>2</sub> and Pu(III) is observed.

**Disproportionation of Pu(V).** Pu(V) can disproportionate to Pu(IV) and Pu(VI) under acidic conditions according to reaction 4 above, which has a second order dependence on the Pu(V) concentration. Thus, the rate of the disproportionation reaction should increase with increasing plutonium concentration. The conceptual model supporting disproportionation of Pu(V) as a mechanism for the surface-mediated reduction of plutonium is that relatively high Pu(V) concentrations exist at the mineral surface due to accumulation and sorption of Pu(V). Disproportionation could occur either on the mineral surface or within the EDL with subsequent sorption of Pu(IV). The exact reaction path would be determined by the relative affinities of Pu(V) and Pu(IV) for the mineral surface.

The disproportionation hypothesis was first put forth by Sanchez et al.,<sup>13</sup> who observed the reduction of Pu(V) in the

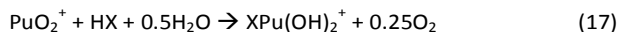
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presence of goethite. They posited that Pu(V) reduction could only be due to incorrect thermodynamic data, trace amounts of Fe(II), radiolysis, or disproportionation. They suggested that disproportionation was the most likely explanation for their results. Around the same time, Keeney-Kennicutt and Morse<sup>28</sup> studied the interactions of Pu(V) with birnessite ((Mn<sup>III</sup>Mn<sup>IV</sup>)<sub>2</sub>O<sub>4</sub>, often reported as δ-MnO<sub>2</sub>) and goethite. Oxidation state analyses show that plutonium associated with goethite is initially 53.8% Pu(IV), 29.5% Pu(V), and 16.7% Pu(VI) at circumneutral pH. As shown in Figure 6, the fraction of Pu(V) associated with the goethite surface decreases as a function of time and there is a corresponding increase in the fraction of Pu(IV) and Pu(VI). This indicates disproportionation of Pu(V) to Pu(IV) and Pu(VI) may occur at the goethite surface.

However, there is a greater body of evidence in the literature which indicates that disproportionation is not a dominant mechanism for the surface-mediated reduction of plutonium. Romanchuk et al.<sup>19</sup> observed that the oxidation state distribution of plutonium associated with hematite was nearly identical for both batch sorption experiments and XAS measurements even though the concentration of plutonium differed by five orders of magnitude ( $3.63 \times 10^{-9}$  M versus  $2.02 \times 10^{-14}$  M). Similar results were presented in studies using Savannah River Site sediments,<sup>18</sup> manganese-substituted goethite,<sup>112</sup> and high-purity quartz.<sup>21</sup> A fourth study by Hixon and Powell<sup>23</sup> definitively shows that the reduction of Pu(V) in the presence of hematite decreases with increasing plutonium concentration. Shaughnessy et al.<sup>14</sup> also eliminated disproportionation as a mechanism for the surface mediated reduction of Pu(V) in the presence of manganite and hausmannite because the amount of Pu(IV) observed at the mineral surface was more than could have been produced from disproportionation.

**Facilitation by proton exchange sites.** On exchangeable clay minerals such as montmorillonite there are two main mechanisms for plutonium sorption and reduction. Ion exchange processes control plutonium behaviour at low pH while surface complexation controls plutonium behaviour at high pH.

Zavarin et al.<sup>20</sup> studied the sorption of Pu(V) to Na-montmorillonite as a function of pH, ionic strength, and time. At pH < 5, where ion exchange is the dominant sorption mechanism, the plutonium sorption rate is inversely related to ionic strength. When the sorption rate constant is instead plotted as a function of the mole fraction of exchangeable H<sup>+</sup>, a one-to-one correlation is found that can be described by reaction 17 where HX represents an exchangeable H<sup>+</sup>.



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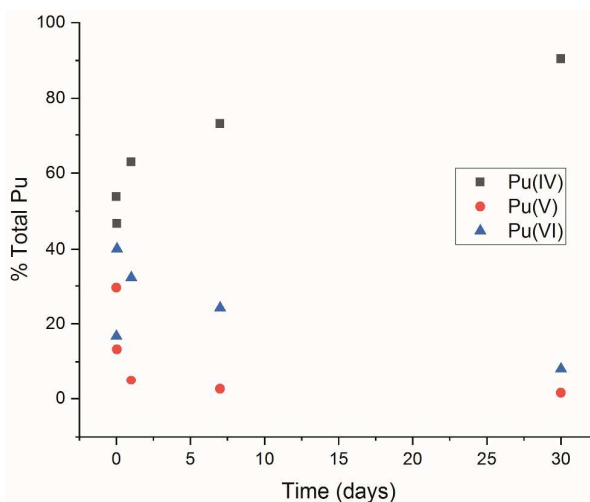


Figure 6 – Oxidation state distribution of plutonium ( $[\text{Pu}]_T = 5 \times 10^{-10}$  M) adsorbed on goethite ( $5 \text{ m}^2 \text{ L}^{-1}$ ) in deionized water equilibrated with calcite and seawater under dark conditions. Data from reference 28.

Reactions such as 17 may be especially important when considering plutonium interactions with whole soils, such as sediments from the Savannah River Site which are rich in kaolinite and chlorite/vermiculite clays,<sup>24</sup> or areas which contain high amounts of soil organic matter.

**Stabilisation of Pu(IV) on the mineral surface due to increased concentration gradient within the EDL.** As evidenced by the discussions above, the reduction of Pu(V) is mediated by the mineral surface. However, the exact mechanism of complex formation depends upon the plutonium/mineral ratio and the total plutonium concentration.<sup>19,22</sup> In the mechanisms for surface-mediated reduction discussed thus far, monomeric surface species complexes are expected to form. However, when the total plutonium concentration exceeds a certain value, the formation of plutonium colloids or other precipitates are often observed associated with the mineral surface.<sup>19,22,23,123,124</sup> The plutonium concentration at which this shift from monomeric to polymeric surface complexes occurs is not well constrained. Romanchuk et al.<sup>22</sup> report a value of  $10^{-9}$  M plutonium in the presence of hematite, whereas Hixon and Powell<sup>23</sup> suggest a slightly higher value of  $10^{-7}$  M plutonium, and Zhao et al.<sup>124</sup> report a value of  $10^{-8}$  M plutonium in the presence of goethite.

At  $10^{-10}$  M total plutonium,  $10 \text{ m}^2/\text{L}$  hematite, and 99% sorption, the concentration of plutonium within 1 nm of the hematite surface is approximately  $10^{-7}$  M (see Supporting Information).<sup>19</sup> Assuming that plutonium was added as Pu(V) and reduction of Pu(V) to Pu(IV) occurs at the mineral surface, the resulting concentration of Pu(IV) exceeds the expected solubility of Pu(IV), which is expected to be  $5 \times 10^{-10} - 6 \times 10^{-8}$  M depending upon pH and temperature.<sup>59,67</sup> The solubility-

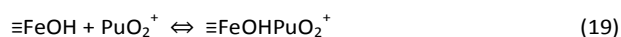
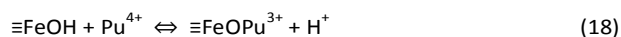
limiting phase is unknown and generally attributed to  $\text{PuO}_{2+x}(\text{s,hyd})$ .

At plutonium concentrations greater than approximately  $10^{-10}$  M, Romanchuk et al.<sup>19</sup> propose that Pu(IV) polymerization may occur due to the high concentration of plutonium near the hematite surface. In systems containing  $4 \times 10^{-10}$  M Pu(IV), a two-step sorption reaction is observed. The first step is attributed to fast sorption of monomeric Pu(IV) to hematite; the second step is attributed to the formation of polymeric Pu(IV). A similar three-step reaction is observed in solutions containing  $4 \times 10^{-9}$  M Pu(VI): fast sorption of Pu(VI), slow reduction of Pu(VI) to Pu(IV), and Pu(IV) polymerization. Leaching tests comparing sorbed plutonium and  $\text{PuO}_{2+x}(\text{s,hydr})$  show that the fraction of leached plutonium as a function of time is the same. At  $\text{pH} > 5$ , plutonium is associated with hematite as Pu(IV) despite the oxidizing conditions of solution ( $E_h = 550 - 850$  mV).

Using high-resolution transmission electron microscopy (HRTEM) and XANES spectroscopy, Romanchuk et al.<sup>22</sup> showed that at concentrations greater than  $10^{-9}$  M, crystalline nanoparticles of  $\text{PuO}_{2+x}(\text{s,hyd})$  are associated with the mineral surface. Similar images were obtained by Hixon and Powell<sup>23</sup> when approximately  $10^{-6}$  M Pu(V) was added to a suspension containing hematite. Plutonium polymerization at the goethite surface yields  $\text{Pu}_4\text{O}_7$  regardless of whether plutonium is added as Pu(IV)<sup>123</sup> or Pu(V).<sup>124</sup> The lattice distortion that occurs in these systems may result in stronger binding of plutonium compared to systems where such distortion is not observed.

**Nernstian favourability of Pu(IV) surface complexes or nanocolloids.** Reduction of Pu(V) may proceed through an energetically-favoured reaction where the free energy ( $\Delta G$ ) of Pu(IV) surface complexes or surface precipitates is lowered sufficiently to raise the reduction potential of the Pu(V)/Pu(IV) couple and favour reduction.<sup>16,21,22</sup> Electrons needed for the reduction reaction would come from water and also produce oxygen gas.

Hixon et al.<sup>21</sup> used this hypothesis to support the observed reduction of aqueous Pu(V/VI) to sorbed Pu(IV) in the presence of high-purity quartz and showed, through an example calculation in which Pu(IV) is oxidised by oxygen, that the redox potential of the Pu(V)/Pu(IV) couple would need to be raised by only 0.28 V in order for the Pu(IV) surface complexes to be thermodynamically favourable. Support for this shift comes from equilibrium constants for the surface complexation of Pu(IV) and Pu(V) by goethite, which are  $\log K = 14.33$  and  $\log K = 5.14$  for reactions 18 and 19, respectively.<sup>125</sup>



These two values differ by approximately 9 orders of magnitude and indicate that the formation of Pu(IV) surface complexes is more thermodynamically favourable than the formation of Pu(V) surface complexes. Further support comes from calculations showing that the stability field of sorbed Pu(IV) at  $\text{pH} < 7$  is increased relative to the stability field of aqueous Pu(IV) in the presence of illite and kaolinite.<sup>126,127</sup>

In particular, this surface-mediated reduction hypothesis explains observations of plutonium reduction on mineral surfaces that do not contain an obvious electron donor, such as quartz<sup>21</sup> and amorphous silica.<sup>111</sup> It also tends to describe the reduction of plutonium in systems with high total plutonium concentrations. Hixon and Powell<sup>23</sup> studied the mechanism and rates of Pu(V) reduction on hematite as a function of total plutonium concentration ( $10^{-8} - 10^{-6}$  M). At plutonium concentrations less than approximately  $10^{-7}$  M, reduction was attributed to trace amounts of Fe(II) in the hematite structure. The reduction of plutonium at higher concentrations was attributed to the formation of  $\text{PuO}_{2+x}(\text{s,hyd})$  nanoparticles or a Pu(IV) monomeric surface complexes, which was driven by the Nernstian favourability of the Pu(IV) species. Emerson and Powell<sup>25</sup> also attributed the reduction of Pu(V) in the presence of hematite nanoparticles at high plutonium surface loadings (22 mg Pu per g of hematite) to the thermodynamic favourability of Pu(IV)-hydroxide surface complexes or Pu(IV) precipitates.

Of all the hypotheses for the surface-mediated reduction of plutonium, the Nernstian favourability of Pu(IV) surface complexes or nanocolloids offers the greatest opportunity for future research, as the redox potential of the Pu(V)/Pu(IV) couple has not been measured in the presence of a mineral surface and currently there is no obvious method of proving the hypothesis to be true.

## Summary and Recommendations

In order to predict the behaviour of plutonium at the mineral-water interface, it is important to understand the speciation of plutonium in the aqueous phase. Plutonium can be complicated to work with because it is found in four primary oxidation states – Pu(III), Pu(IV), Pu(V), and Pu(VI). Multiple redox states can coexist in solution due to the similarity in redox potentials and the disproportionation of Pu(IV) and Pu(V). While Pu(III) is generally considered to be unstable except in low pH, reducing environments, several studies have highlighted that this is not a valid assumption and that further studies are warranted.<sup>42-44</sup> Pu(V) is the weakest complexing and most soluble oxidation state of plutonium and is thus generally assumed to be the most mobile plutonium oxidation state. Conversely, Pu(IV) forms strong complexes, has a high sorption affinity, and low solubility causing mononuclear Pu(IV) to be the least mobile plutonium species. Therefore, surface-mediated reduction of Pu(V) to Pu(IV) serves to minimize the mobility of plutonium in aqueous environments.

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Notable exceptions to this generalized statement are cases where Pu(IV) is transported as an organic ligand complex or colloidal species.<sup>81,83,84,128</sup>

We summarized the literature that supports or refutes each of the seven hypotheses for the surface-mediated reduction of plutonium. *Radiolysis at the mineral surface* was determined to be an unlikely cause of surface mediated Pu(V) reduction, but was supported by one research study. Further studies may be warranted to corroborate this result. *Electron transfer via ferrous iron or Mn(II) at the mineral surface* is a plausible mechanism, but will be difficult to disprove until lower detection limits for Fe(II) and Mn(II) exist. There are a larger number of studies looking at the behaviour of plutonium at iron-bearing mineral surfaces as compared to manganese-bearing minerals. Further studies with manganese minerals are warranted because in a micro-X-ray fluorescence ( $\mu$ XRF) analysis of Yucca Mountain Tuff, Duff et al.<sup>116</sup> found that sorbed plutonium was preferentially associated with manganese oxide minerals and smectites as opposed to iron oxide phases or zeolites. Manganese oxide minerals can initially facilitate both oxidation and reduction of plutonium, but Pu(IV) becomes the dominant solid phase species associated with the mineral surfaces at long time periods. Further experiments focusing on plutonium interactions with manganese-bearing minerals are warranted. *Electron shuttling due to the semiconducting properties of the mineral* remains a plausible hypothesis, but only applies to semiconducting minerals. Similarly, *reduction facilitated by proton exchange sites* is only valid for soils and sediments that contain high concentrations of clay minerals. *Stabilization of Pu(IV) due to an increased concentration gradient within the electrical double layer* attempts to explain the shift from monomeric to polymeric surface complexes and is supported by data from HRTEM and XAS. However, the currently available, peer-reviewed studies primarily focus on iron oxide minerals. The *Nernstian favourability of Pu(IV) surface complexes or nanocolloids* may be the most important hypothesis for minerals that do not contain an obvious electron donor and provides the greatest opportunity for future work. Finally, the *disproportionation of Pu(V)* is the only hypothesis to be definitively disproven in multiple studies across a suite of pure mineral phases.

We prefer to identify "the reason" or "the mechanism" that controls processes, such as the behaviour of plutonium at the mineral-water interface. However, it is much more likely that some combination of factors or mechanisms contributes to the surface-mediated reduction, or that the mechanism(s) will change depending upon the solid phase. For example, it is reasonable to think the electron transfer or electron shuttling are the dominant mechanisms for the surface-mediated reduction of plutonium in the presence of iron (oxyhydr)oxide minerals whereas other mechanisms likely dominate in silica-based systems.

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This review maintained a focus on the interactions of plutonium with pure mineral phases. However, in environmental systems one must also consider other phenomena, such as precipitation and dissolution of plutonium solid phases, the influence of organic ligands and natural organic matter, and the influence of microorganisms.

These factors have the potential to interact with plutonium in the aqueous phase or otherwise prevent plutonium sorption to soils and sediments, thereby enhancing plutonium mobility in the subsurface environment. Therefore, intensive studies on the mechanisms, thermodynamics, and kinetics of these processes will also be needed to inform a global conceptual model of plutonium subsurface behaviour.

The development of field-scale models describing plutonium transport in the environment will likewise need to consider both near-field and far-field environments. Under near-field conditions, we can expect, among other things, high plutonium concentration, ionic strength, temperature, and radiation fields. Spectroscopic studies will be useful for describing these systems. However, plutonium concentrations in the far-field environment are significantly lower (see Table 5), and are generally even several orders of magnitude lower than the studies presented in this review. These are the concentrations that future studies need to be focused on, since these are the concentrations that will directly affect human health and safety. The major challenge will be developing methods with trace- and ultra-trace-level detection limits so that such studies can produce reliable results.

Table 5 – Concentrations of plutonium in groundwater at US Department of Energy sites and Russia.

Site	Observed [ <sup>239</sup> Pu] (M)	Reference
Hanford, WA 100 K-area	$7 \times 10^{-18} - 7 \times 10^{-20}$	Dai et al. <sup>129</sup>
INEL, ID Chemical processing plant	$2 \times 10^{-17}$	Cleveland and Rees <sup>130</sup>
LANL, NM Mortandad canyon	$3 \times 10^{-12} - 1 \times 10^{-14}$	Penrose et al. <sup>82</sup>
Urals, Russia Mayak Production Assoc.	$5 \times 10^{-14} - 9 \times 10^{-12}$	Novikov et al. <sup>84</sup>
NTS, NV ER-20-5 Well cluster	$1 \times 10^{-14}$	Kersting et al. <sup>83</sup>
SRNL, SC F-area seepage basin	$2 \times 10^{-13} - 9 \times 10^{-13}$	Kaplan et al. <sup>131</sup>

### Conflicts of interest

There are no conflicts to declare.

### Acknowledgements

This research was supported by the Subsurface Biogeochemical Research Program of the U.S. Department of Energy's Office of Biological and Environmental Research under grant award number DE-SC0004883.

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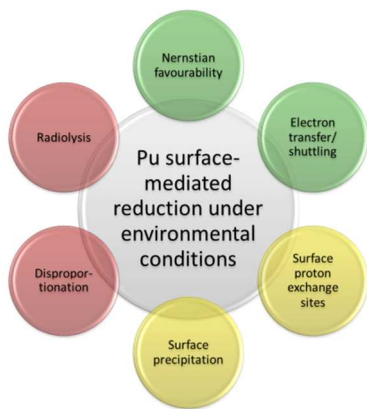


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Evaluation of the seven proposed mechanisms for the surface-mediated reduction of Pu(V/VI).