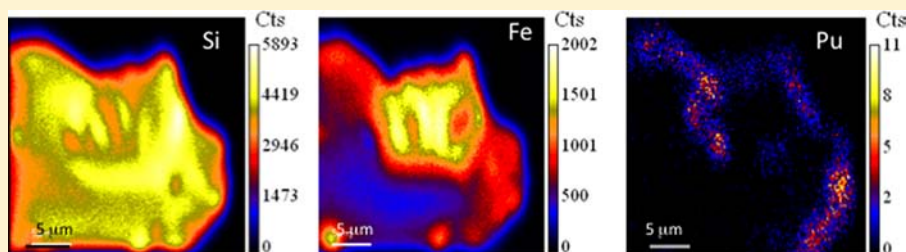


## Plutonium Transport in the Environment

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**ABSTRACT:** The recent estimated global stockpile of separated plutonium (Pu) worldwide is about 500 t, with equal contributions from nuclear weapons and civilian nuclear energy. Independent of the United States' future nuclear energy policy, the current large and increasing stockpile of Pu needs to be safely isolated from the biosphere and stored for thousands of years. Recent laboratory and field studies have demonstrated the ability of colloids (1–1000 nm particles) to facilitate the migration of strongly sorbing contaminants such as Pu. In understanding the dominant processes that may facilitate the transport of Pu, the initial source chemistry and groundwater chemistry are important factors, as no one process can explain all the different field observations of Pu transport. Very little is known about the molecular-scale geochemical and biochemical mechanisms controlling Pu transport, leaving our conceptual model incomplete. Equally uncertain are the conditions that inhibit the cycling and mobility of Pu in the subsurface. Without a better mechanistic understanding for Pu at the molecular level, we cannot advance our ability to model its transport behavior and achieve confidence in predicting long-term transport. Without a conceptual model that can successfully predict long-term Pu behavior and ultimately isolation from the biosphere, the public will remain skeptical that nuclear energy is a viable and an attractive alternative to counter global warming effects of carbon-based energy alternatives. This review summarizes our current understanding of the relevant conditions and processes controlling the behavior of Pu in the environment, gaps in our scientific knowledge, and future research needs.

### INTRODUCTION

As the world's energy needs escalate and evidence for anthropogenic global warming continues to mount, the pressure has intensified to reevaluate nuclear energy as an alternative to the burning of fossil fuels.<sup>1</sup> Nuclear energy has the advantage of producing large amounts of electricity without significantly increasing carbon dioxide emissions, yet many are concerned with potential health and environmental risks. The recent reactor meltdown at the Fukushima Daiichi nuclear power plant in Japan in 2011, following events at Chernobyl, Russia, in 1986, Three Mile Island, U.S., in 1979, and Windscale Fire, England, in 1957, has put the world on notice that large-scale nuclear disasters can and do still happen. Although the health risks and environmental damage from Fukushima Daiichi are still unfolding, this most recent nuclear disaster has had a chilling effect on the global nuclear industry, causing many countries to rethink their nuclear energy policy.

A significant part of current discussions pivot on the inability to convince a skeptical public that nuclear reactors can be effectively and safely operated and the radioactive waste isolated from the biosphere for the thousands of years necessary to allow its radioactive decay. There are currently over 60000 t of spent nuclear fuel stored temporarily at nuclear power plants across the U.S.<sup>2</sup> with no permanent storage solution. As a

result, most spent nuclear fuel remains at nuclear power plants stored in above-ground temporary storage facilities, in either cooling pools or dry storage casks, waiting for a final solution to emerge for permanent storage. Whether or not future U.S. policy involves the direct disposal or reprocessing of spent nuclear fuel, there is a need for an integrated strategy to expedite progress toward a safe permanent storage facility or facilities.<sup>3</sup> Even optimistic estimates for recycling nuclear fuel and reducing the nuclear waste will still require a permanent storage facility.<sup>4</sup>

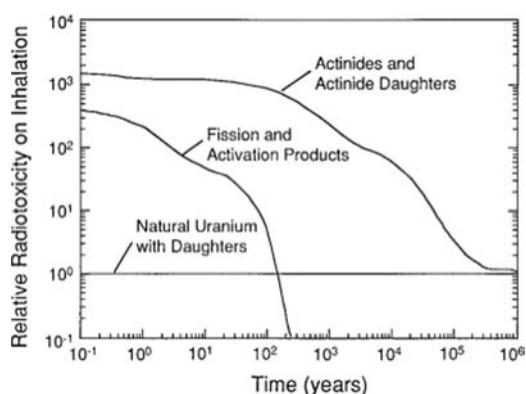
Significant uncertainty remains on how to safely store long-lived, toxic radionuclides for extended time periods. Although high-level waste contains high-activity and long-lived fission products, it is the actinides that will constitute the majority of the dose (radiotoxicity) after just a few hundred years<sup>5,6</sup> (Figure 1). Both the abundance and long half-lives of <sup>239</sup>Pu (half-life  $2.41 \times 10^4$  years) and <sup>237</sup>Np (half-life,  $2.14 \times 10^6$  years) make these radionuclides significant long-term dose contributors for any geologic repository. In 2010, the global inventory of plutonium (Pu) was estimated at  $\sim 1900$  t, with

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**Figure 1.** Relative radiotoxicity upon inhalation of spent nuclear fuel with a burnup of 38 MW·days/kg of U versus time. The radiotoxicity values are relative to the horizontal line showing the quantity of original U ore and demonstrate the importance of actinides in contributing to the total hazards associated with spent nuclear fuel over long-time scales. Reprinted with permission from ref 5. Copyright 1999 National Academy of Sciences.

expected yearly increased contributions of 70–90 t from the nuclear fuel industry.<sup>7,8</sup> In 2012, further accounting estimated that this global inventory consisted of about 500 t of separated Pu, split nearly equally between the civilian nuclear power industry and weapons-related activities.<sup>9</sup>

The current U.S. plan is to bury the nuclear waste deep below the ground surface (bgs) in a highly engineered barrier system and use the natural surrounding host rock as a secondary containment. The U.S. has no current plans to reprocess spent nuclear fuel. Developing a credible strategy for isolating and safely storing high-level nuclear waste is one of the most pressing environmental challenges of the 21st century. Without strong scientific assurances that the current stockpile of Pu can be effectively isolated from the biosphere, the American public will continue to believe that nuclear waste disposal is an unsolvable problem and developing a coherent long-term energy policy will remain elusive.

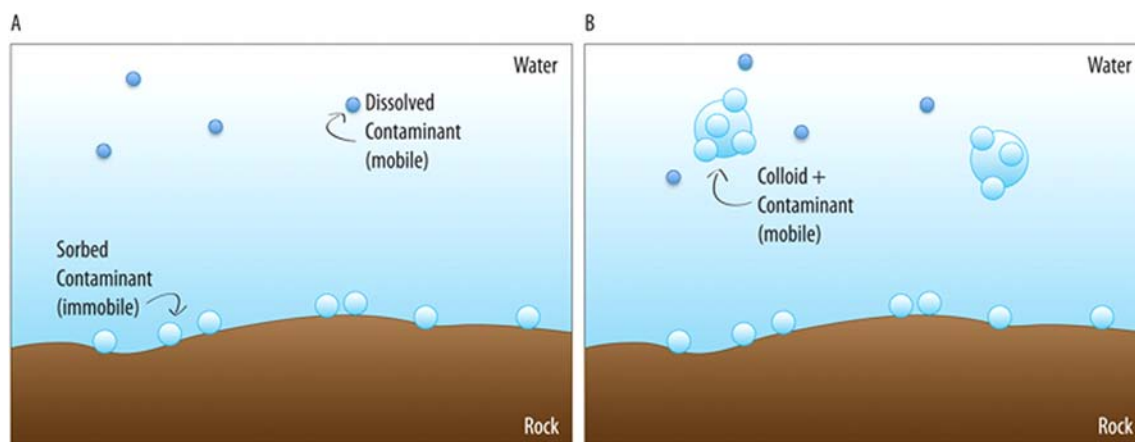
This article focuses on the relevant conditions and processes controlling the behavior of Pu in the environment, current gaps in our scientific knowledge, and future research needs. Several

well-studied field sites are presented to illustrate how Pu has behaved under different field conditions. The sites chosen are not an exhaustive group but were chosen to provide examples where Pu has migrated under several different complex biogeochemical and hydrogeologic environments.

## ■ THE HISTORY OF PU

The vast majority of Pu found in the environment is man-made as a byproduct of nuclear fission occurring in nuclear reactors, and only trace quantities have been detected as primordial in nature. In 1960, <sup>244</sup>Pu ( $t_{1/2} = 80 \times 10^6$  years) was hypothesized and later confirmed to exist during the formation of the solar system to explain the excess xenon isotopes measured in an achondritic meteorite.<sup>10–12</sup> Approximately 2 billion years ago, uranium (U) deposits at the Oklo and Bagombe mines in the Republic of Gabon sustained natural fission reactions that produced Pu by neutron capture of U isotopes.<sup>13</sup> It is estimated that these natural fission reactors produced about 2.5 t of Pu that has since decayed away.<sup>14</sup> These examples demonstrate that Pu has been produced in nature in ancient events but only under rare circumstances and with only trace primordial amounts existing today.<sup>15</sup> The worldwide inventory of Pu that exists today is overwhelmingly man-made.

Pu ( $t_{1/2}$  of <sup>238</sup>Pu = 87.7 years) was first synthesized by Glenn Seaborg, Edwin McMillan, Joseph Kennedy, and Arthur Wahl at University of California at Berkeley in 1940 by bombarding <sup>238</sup>U with deuterons.<sup>16,17</sup> In 1941, the same team successfully chemically separated and identified <sup>239</sup>Pu (half-life  $2.4 \times 10^4$  years) by bombarding <sup>238</sup>U with neutrons but was only able to publish their results after the war in 1946.<sup>18–20</sup> Today, the global inventory of Pu released to the environment comes from human activities surrounding weapons production and the nuclear power industry. These activities include the manufacturing of nuclear weapons, atmospheric and underground nuclear weapons testing, intentional and accidental disposal of high-level waste and solvents from nuclear fuel processing, atmospheric discharges from nuclear power plants, and accidents at nuclear power plants.<sup>21</sup> Runde and Neu<sup>21</sup> give a comprehensive review of worldwide releases of Pu and other actinides.



**Figure 2.** Cartoon depicting contaminant transport in two- and three-phase systems: (A) Contaminant transport in a two-phase system. Dark-blue circles are dissolved species (mobile), and larger light-blue circles are sorbed to the host rock (immobile). (B) Contaminant transport in a three-phase system. Contaminants that are sorbed to the host rock can also attach to the mobile colloid and migrate with groundwater. Modified from a figure appearing in ref 119. As shown, in a two-phase system, only the dissolved contaminant is transported in groundwater, whereas in a three-phase system, the low-solubility, strongly sorbing contaminant can sorb to a colloid and migrate.

## ■ THE FATE AND TRANSPORT OF PU

The fate and transport of Pu depends not only on the initial chemical form at the source but also on the geochemistry and hydrology of the source location and subsequent down-gradient transport pathways. Over the last 10–15 years, there has been a paradigm shift in our understanding of Pu in the environment. Once thought to be immobile in the subsurface because of its very low solubility and high surface reactivity, Pu has now been shown to migrate at low concentrations with naturally occurring submicrometer particles, called colloids.<sup>22</sup> Colloidal transport of Pu in both surface water and groundwater has been documented at field sites, including the Nevada Test Site<sup>22</sup> and the Rocky Flats Environmental Technology Site.<sup>23,24</sup> Furthermore, Pu sorbed to iron oxide colloids has been detected over 4 km from its original source of origin at the Mayak Site in Russia.<sup>25</sup> All three studies indicate that the Pu associated with mobile colloids has moved on the scale of kilometers. Laboratory experiments have also confirmed that colloids (both inorganic or organic material) can accelerate the transport of contaminants through both porous and fractured media.<sup>26,27</sup> Colloid-facilitated transport is not a new idea;<sup>28</sup> however, its importance in the transport of actinides and other low-solubility contaminants has only gained acceptance in recent years.<sup>22,28–32</sup>

Observations of colloid-facilitated Pu transport from field studies helped to strengthen a new conceptual transport model whereby the classical two-component system of dissolved and stationary phases (Figure 2A) was expanded to a three-component system (colloids, dissolved, and stationary phases; Figure 2B). Strongly sorbing contaminants, such as Pu, can either migrate as a dissolved aqueous species, sorb to mobile colloids in groundwater, or become immobilized by attaching to the host rock or soil. Aqueous species and mobile colloids may also become immobilized by direct attachment to the host rock or soil or by removal of colloids via filtration.<sup>30,31,33</sup> The ability of Pu to strongly adhere to inorganic minerals and organic material can both ultimately enhance (mobile colloids) and reduce (stationary soil and host rocks) the migration of Pu. Modeling this behavior requires a three-component system, and using a two-component model could severely underestimate the transport behavior of contaminants associated with colloidal particles. Even with three-component models, a better molecular-level understanding of the dominant biogeochemical mechanisms controlling Pu–aqueous surface interactions is currently lacking and is needed to predict long-term migration under a range of geochemical environments. Transport models are not yet robust enough to be able to predict how much or how fast Pu will migrate. Equally pressing is the need to understand the biogeochemical conditions in which Pu transport will be severely limited.

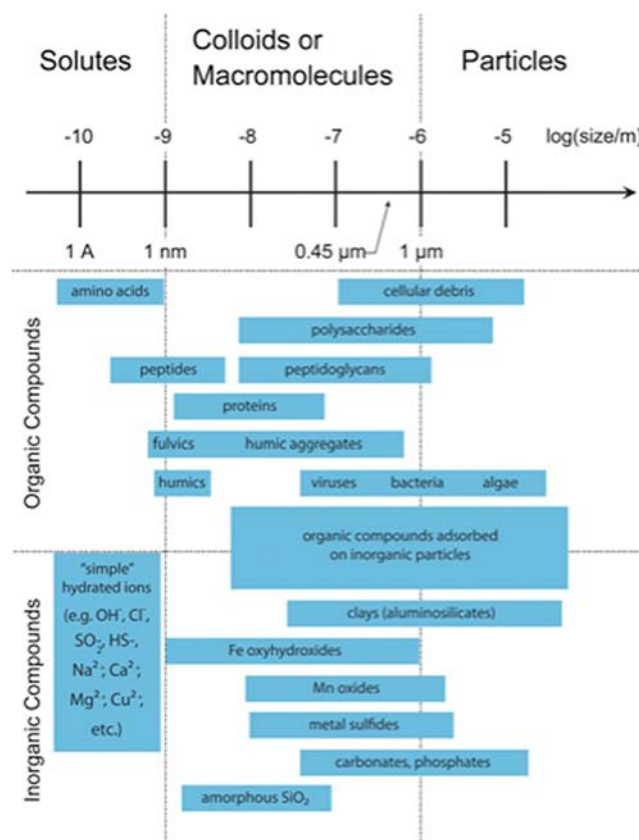
## ■ NATURAL COLLOID CHARACTERISTICS

Colloids are defined as particles between 1000 and 1 nm<sup>34,35</sup> and are ubiquitous in both groundwater and surface water.<sup>31,36</sup> They are chemically, structurally, and temporally complex organic, inorganic, or microbial species of both natural and anthropogenic origin and can remain suspended as a result of their small size and low settling velocity.<sup>37</sup> Organic coatings on inorganic minerals have been shown to increase the stability of the multiphase colloids in solution.<sup>38</sup> Because of their high surface area per unit mass ( $10^4$ – $10^5$  m<sup>2</sup>/kg) and the high density of surface functional groups, they have the potential to

sorb a significant amount of contaminants. Contaminants, such as Pu, that sorb to natural inorganic or organic colloids are sometimes referred to as mineral colloids, organic colloids, or more generally pseudocolloids.<sup>32</sup> At high concentrations, Pu can also hydrolyze and precipitate from solution to form a plutonium oxide colloid, referred to as an intrinsic or Eigen colloid.

The presence of colloids does not necessarily guarantee the transport of Pu or other strongly sorbing radionuclides. Other factors such as colloid filtration, stability, groundwater flow rate, groundwater chemistry, and desorption/dissolution rates of Pu to pseudocolloids are all important in determining whether transport will occur. Colloids (pseudo or intrinsic) have the potential to greatly increase the transport of contaminants such as Pu, but first the colloids must exist and remain stable, and in the case of pseudocolloids, the Pu must remain attached (e.g., slow desorption).<sup>31,39</sup>

With renewed recognition that colloids represent a potential contaminant transport pathway, scientists have recently made significant contributions to understanding their natural abundance, size, composition, stability, flow rate, and sorption and desorption/dissolution rates under a range of geochemical environments in both porous media and fractured rock.<sup>31,39,40</sup> The kinetics of Pu sorption/desorption on colloids will largely determine its transport ability.<sup>26</sup> Natural colloids are found in all water and composed of inorganic minerals, organic species, and microorganisms. Figure 3 shows a generalized size distribution of the different types of natural colloids.<sup>33</sup> Inorganic colloids generally consist of clays, zeolites, iron



**Figure 3.** Size distribution of different types of environmental dissolved species, organic and inorganic colloids, macromolecules, and particles. Modified from a figure appearing in ref 33.



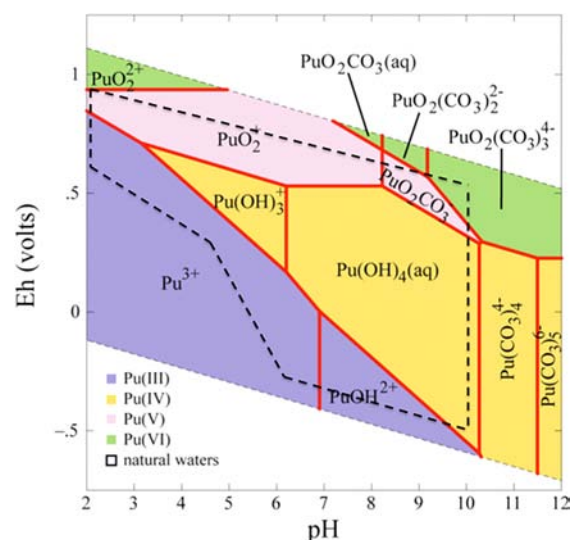
oxides, and carbonates, reflective of secondary minerals in equilibrium with their host rock and groundwater environment.<sup>29</sup> Colloids can have a range of sizes, making it difficult to determine the size distribution precisely. This is particularly true for natural organic matter (NOM).<sup>41</sup> Considerable effort has also been invested in measuring the concentration of natural colloids in different hydrogeochemical environments to estimate the maximum colloidal mass available for Pu sorption and potential transport. The natural colloidal loads measured in a variety of different geologic locations ranges from less than 1 mg/L to several hundreds of milligrams per liter.<sup>38,42</sup> In general, deeper groundwater has fewer colloids than shallower systems. In deep groundwater collected from fractured granite at the Grimsel Test Site, Switzerland, colloid concentrations were  $\leq 1$  mg/L.<sup>36</sup> Colloid concentrations measured from unpumped flowing groundwater in an abandoned mine in Goesdorf, Luxembourg, were between 0.12 and 0.029 mg/L.<sup>43</sup> The low concentrations ( $\sim 1$  mg/L) from both the Grimsel Test Site and the Goesdorf mine may be more reflective of ambient colloid concentrations compared to colloid concentrations measured from pumped well waters, where the effect of pumping has been shown to increase the colloid concentration.<sup>42</sup> Measuring colloid concentrations in water by either not pumping or using very low flow rates reduces the chance of artificially disturbing the groundwater system, providing the most reliable colloid concentrations.<sup>42</sup>

For steady-state conditions, the chemical composition of water plays a major role in determining the stability of inorganic colloids. Most field and laboratory studies have demonstrated that lowering the ionic strength of groundwater results in the generation and stability of inorganic colloids, whereas increasing the ionic strength tends to promote coagulation and removal from the system.<sup>44</sup> Geochemical conditions that reduce the stability of inorganic or organic colloids would have the desired result of limiting colloid-facilitated contaminant transport.

In the presence of stable natural colloids, colloid-facilitated transport of Pu in near- and far-field environments is governed by a strong affinity of Pu for the colloid surface and the reversibility of the reaction. Stumm and Morgan provide a review of the fundamental sorption processes at the solid–water interface.<sup>33,35</sup> However, the reversibility of these processes has not been scrutinized in sufficient detail even though it is expected to control the effectiveness of colloid-facilitated transport. Not surprisingly, this topic has become a subject of active research in recent years.<sup>45</sup>

## ■ AQUEOUS PU CHEMISTRY

Pu can dissolve as an aqueous ion, precipitate out of solution, attach (sorb) to an immobile surface, or sorb to a mobile colloid (Figure 2). To a large extent, the reaction chemistry of Pu in a given aqueous system will control its mobility and transport. The reaction chemistry of Pu (i.e., aqueous speciation, solubility, sorption affinity, redox chemistry, and affinity for colloidal particles) is strongly controlled by its oxidation state.<sup>46</sup> Pu can exist in as many as four oxidation states at environmentally relevant solutions conditions (3+, 4+, 5+, or 6+). Figure 4 is a generalized Eh–pH diagram that shows the dominant Pu species that exist for a range of Eh and pH values for a given water composition (calculated in the present of air). The black dashed line in Figure 4 outlines the possible Pu oxidation states for a range of common natural waters. Pu(IV) and Pu(V) are the dominant oxidation states in



**Figure 4.** Eh–pH diagram of Pu calculated for a  $\text{NaHCO}_3$  solution in equilibrium with  $10^{-3.4}$  bar of  $\text{CO}_2$  at  $25^\circ\text{C}$ . Thermodynamic data used to generate the diagram are from Guillaumont and colleagues.<sup>120</sup> The dashed black line represents the range of common natural waters, which include multiple oxidation states of Pu. Diagram from a personal communication by M. Zavarin.

most waters, although Pu(III) and Pu(VI) also exist. Pu(VI) is stable in highly oxidized waters with high ionic strengths and Pu(III) under more reducing conditions. In the neutral region (pH 6–8), under oxidizing conditions only a small change in Eh can result in a change in the oxidation state of Pu, influencing its solubility and chemical reactivity in both the solution and solid phases.<sup>46,47</sup> The oxidation state of Pu greatly controls its behavior in the environment.

In general, the oxidizing conditions in natural waters vary as follows: rain > ocean water > surface waters > groundwater > reducing groundwater. Thus, the oxidation state of Pu should be highest in rain water and lowest in reducing groundwater. Given the overlap of these hydrologic regimes, however, mixed oxidation states of Pu commonly exist in natural waters. In seawater and surface waters in contact with the atmosphere, Pu exists in its more oxidized form, Pu(V). In groundwater, Pu(V) and Pu(IV) are the dominant oxidation states.<sup>48,49</sup> At pH values below 3, Neck and colleagues measured equimolar concentrations of Pu(III) and Pu(IV) in solution.<sup>58</sup> At environmental concentrations and neutral-to-low pH values, Pu(V) has been shown to be the dominant dissolved aqueous species under oxidizing conditions.<sup>46,50,51</sup> Pu(V) has also been found to be the predominant aqueous species in the presence of mineral suspensions.<sup>52–54</sup>

The solubility of Pu in water is strongly dependent on its oxidation state. The solubility of Pu follows the effective charge of the actinide ions and its affinity for complexation. In general, Pu(V) and Pu(VI) are more soluble and Pu(IV) and Pu(III) are more insoluble. For example, under oxidizing conditions, at near-neutral pH without complexing ligands in solution, Neck and colleagues determined the solubility of Pu(IV) to be  $\sim 10^{-14}$  M and Pu(V) to be  $\sim 10^{-8}$  M. Pu(IV) is sparingly soluble and relatively immobile and can exist as a free ion, but it tends to hydrolyze in solution. In contrast, Pu(V) is more soluble than Pu(IV), is more mobile, does not form strong complexes, and instead forms actinyl ions ( $\text{PuO}_2^+$ ) in solution.

Just knowing the oxidation state of Pu in solution is not enough to predict its behavior because its behavior is strongly influenced by both the species in the aqueous system and interactions with the surrounding solids (immobile solids and mobile colloidal material). Pu(IV) readily sorbs to inorganic and organic surfaces. To model and predict the reaction chemistry of Pu, we must know the surface composition, surface structure, solubility product of the controlling solid, oxidation state, concentration of the individual inorganic and organic ligands, stability constants for the Pu ligand complexes, and compositions of the dissolved aqueous species. In addition, the ultimate transport of Pu will most likely be controlled by the reactions of Pu with the particulate (immobile and mobile) colloidal surfaces and the aqueous system.

### ■ AQUEOUS COMPLEXATION REACTIONS WITH PU: INORGANIC

Pu can also form stable aqueous complexes with naturally occurring inorganic and organic ligands in solution, affecting its solubility, colloid formation, and sorption behavior. The mobility of Pu may be enhanced if it forms stable aqueous inorganic or organic complexes and its solubility is increased. Inorganic ligands, such as hydroxide, carbonate, nitrate, phosphate, and sulfate, with the potential to complex Pu are found in most natural waters. In keeping with effective charge considerations, Pu(IV) forms the strongest aqueous complexes and Pu(V) has the weakest complexation affinity. Carbonate and hydroxide are the two most important environmental inorganic ligands found in natural waters.<sup>47,48,55</sup> Pu(IV) strongly complexes to hydroxide (hydrolysis) and forms stable Pu(OH)<sub>4</sub> complexes in solution (Figure 4). Even in acidic solutions, Pu(IV) is not present as a free ion. Hydrolysis begins at pH ~ 1 and progresses in a stepwise manner until the Pu(OH)<sub>4</sub>(aq) species is dominant at pH > 4. At higher concentrations, hydrolysis products of Pu(IV) can also polymerize and form colloidal or macroscopic precipitates (intrinsic colloids).<sup>56–58</sup> Carbonate is found in a range of concentrations in almost all natural waters and competes with hydroxide to complex Pu ions. For example, Pu(IV) plus CO<sub>3</sub><sup>2-</sup> can readily complex to form PuCO<sub>3</sub><sup>2+</sup> in solution, increasing the concentration of Pu in solution compared to carbonate-free solutions.<sup>59</sup>

### ■ ORGANIC MATTER INTERACTION WITH PU: AQUEOUS SPECIES AND COLLOIDS

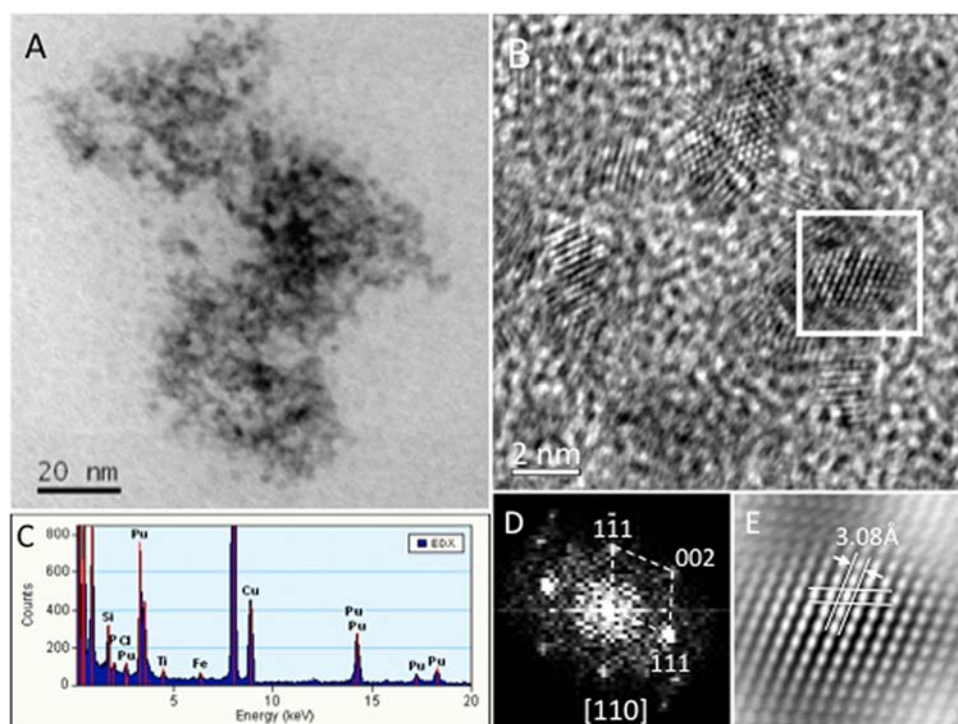
Organic matter is ubiquitous in shallow groundwater and surface water and can bind to metal ions to produce Pu complexes in solution or pseudocolloids. NOM results from the mechanical or microbial breakdown of plants and animals, microbial exudates, or turnover in microbial populations. Organic matter is a mixture of complex organic molecules that can exist as both an aqueous species and organic nanocolloids, which are both able to strongly complex or bind to Pu. NOM can consist of relatively simple organic acids (e.g., citric acid) to more complex microbial exudates (e.g., siderophores and extracellular polymeric substances) to large macromolecules [e.g., humic and fulvic acids (HA and FA)]. The “average structure” of humic substances has a large hydrodynamic range from 1 nm to hundreds of nanometers<sup>41,60,61</sup> (see Figure 3). HAs and FAs can be described as a distribution of high-molecular-weight compounds that behave as particles and low-molecular-weight compounds that behave

as aqueous ligands, respectively. Categorizing the interaction of Pu with an organic material as either an aqueous complex (dissolved) or a nanocolloid is challenging because organic material ranges in size and does not have a readily defined structure. Organic matter can range from low-molecular-weight dissolved organic matter (DOM) to small colloids—macromolecules (~1 nm) to nanocolloids (~1–10 nm) or larger (hundreds of nanometers)—and often working at these size fractions is difficult. Depending on the oxidation state of Pu, the molecular weight of the organic complex, ionic strength, water chemistry, and mineral/soil composition and structure, a Pu–organic complex will either precipitate as a nanocolloid or persist in solution as DOM. Determining the formation, structure, stability, and mobility of organic matter that exists at the intersection of dissolved ions, macromolecules, and small nanocolloids is an active area of research with important implications for understanding far-field transport. For this review, the distinction between dissolved and colloidal organic matter will be based on the size. Organic material of less than 1 nm will be discussed as an aqueous species with the recognition that much work is needed to understand how macromolecules and nanocolloids at the 1–5 nm range behave structurally and chemically in aqueous systems.

The current understanding of humic substances and their importance to enhanced radionuclide transport has been recently recognized.<sup>39,60,62–64</sup> Pu was found to bind to humic colloids for very long periods of time, enhancing the transport of Pu in groundwater.<sup>65</sup> In general, metals were found to sorb mainly to humic colloids in the pH region below the sorption edge.<sup>66</sup> The sorption of metals to humic colloids was also found to increase with increasing ionic strength.<sup>60</sup> Humic colloids can also affect the oxidation state of redox-sensitive actinides. In the presence of HAs, Pu was observed to rapidly reduce from Pu(VI) and Pu(V) to Pu(IV) and Pu(III).<sup>67</sup> While the desorption of Pu from organic colloids is likely to control the transport behavior, results from experiments are limited in the literature. As an analogue for Pu(IV) and Th(IV) was presorbed to humic colloids at pH 8 and then desorbed by acid treatment. Desorption was incomplete, with 10–50% remaining on the humic colloids, suggesting that long-term sorption of An(IV) cations to humic colloids could be a significant pathway for contaminant transport.<sup>68</sup>

### ■ INORGANIC COLLOID INTERACTIONS WITH PU

Inorganic colloids are produced as a result of the geochemical alteration of host rock minerals and soil and the formation of secondary mineral precipitates. Inorganic colloids may also be resuspended in solution as a result of changes in the water composition and physical groundwater flow mechanisms. Over the last few decades, numerous studies have investigated the fundamental behavior of Pu interactions with the common inorganic minerals, clays, zeolites, quartz, iron oxides, and carbonates. Pu(IV) has been shown to attach (sorb) to a variety of common mineral surfaces, reaching equilibrium within a few hours to weeks (e.g., iron oxides, manganese oxides, clays, quartz, and brucite).<sup>46,53,54,69–73</sup> The rate and strength of the sorption is a function of the pH, ionic strength, mineral composition, and point of zero charge of the sorbent. As the pH increases, mineral surfaces deprotonate and become more negatively charged, which increases the affinity of positively charged Pu aqueous species. Conversely, low sorption of Pu is observed at low pH, where the surface becomes more positively charged.



**Figure 5.** TEM images of intrinsic Pu nanocolloids. (A) Low-magnification bright-field TEM image of a cluster of nanocolloids on a carbon film. (B) HRTEM image showing an individual nanocolloid structure highlighted in a white box. (C) Energy-dispersive X-ray spectrum of the Pu nanocolloids in part A. (D) Fast Fourier transform of a Pu nanocolloid from the box in part B, showing the PuO<sub>2</sub> fcc structure. (E) Filtered image of the Pu colloid in the box in part B, showing a lattice image of PuO<sub>2</sub> fcc nanocolloids. The electron beam is parallel to the [110] zone. Reprinted with permission from ref 89. Copyright 2011 American Chemical Society.

In contrast to Pu(IV), the rate of sorption of Pu(V) is slow and has been shown to result from the surface-mediated reduction of Pu(V) to Pu(IV).<sup>52,54,70,73–77</sup> Although Pu sorbs to all minerals, in general redox-reactive minerals (e.g., manganese oxide and iron oxide) sorb Pu faster and more strongly than non-redox-reactive minerals (e.g., quartz, gibbsite, and clay). This reduction has been documented even on minerals that would typically be considered as oxidizing or redox-inactive such as pyrolusite, birnessite, hematite, goethite, montmorillonite, silica, and gibbsite. The mechanism for this reduction has not been positively identified and is an area of active research.

Just as important as understanding how quickly Pu will attach to inorganic colloids is determining how readily it will desorb. The rate of Pu desorption will ultimately control its transport; yet the process is inherently complicated by the multi-component nature of the natural environment. A change in the pH or ionic strength, organic content, rock type, or oxidation state will all influence the desorption behavior of Pu. There are still far fewer colloid desorption studies compared to adsorption studies reported in the literature. Those that have been carried out show that the desorption rates of Pu in near-neutral pH are slow but nonzero. Lu and co-workers showed that desorption of Pu from hematite, silica, and smectite was slow, on the order of several months, but not irreversible.<sup>78</sup> If Pu colloid desorption rates are reasonably fast, colloid-facilitated Pu migration from its original source into the far field will be severely limited.

#### ■ MICROBIAL COLLOID INTERACTIONS WITH PU

Microorganisms are ubiquitous in nature, and they also have the ability to alter the chemical speciation, solubility, stability,

and sorption processes of Pu in the environment. Biochemical interactions between radionuclides and microorganisms are also extraordinarily complex and can consist of a number of processes including external cell accumulation (sorption), internal cell accumulation, biomineralization, redox transformations, and ligand complexation.<sup>79</sup> Microorganisms can directly or indirectly affect the redox state of Pu. Sorption of Pu(VI) to bacterial biomass resulted in a reduction to Pu(IV) that was bound to a phosphate group on the cell surface.<sup>80</sup> A slight increase in the microbial respiration was shown to reduce Pu(VI) to Pu(IV).<sup>81</sup> Microbes have also been shown to solubilize Pu because of the production of organic acids.<sup>82,83</sup> A detailed review of radionuclides and their interaction with bacteria and their microbial matter was recently provided by Francis.<sup>84</sup>

#### ■ MULTICOMPONENT COLLOID INTERACTIONS WITH PU

Although many studies have looked at the behavior of radionuclides in both organic and inorganic binary systems separately, organic and inorganic colloids do not exist in isolation. Understanding the interaction of both organic matter and microbes with inorganic surfaces must be tackled in order to understand the behavior of Pu in the complexity of natural systems. Interactions between organic and inorganic colloids greatly influence the behavior of radionuclides, yet limited research has been done on Pu. Humic colloids can fractionate, complicating efforts to understand their sorption mechanism.<sup>60</sup> Recently, Powell and colleagues showed that, in multi-component systems, sorption of Pu to a mineral surface in the presence of HA is usually enhanced at low pH (formation of ternary HA–mineral–metal sorption complexes) and



Table 1. Biogeochemical Parameters of Water and Soil Samples Contaminated with Pu

site	depositional location	depositional location geology	Pu samples	transport distance	organic content (mg of C/L)	pH at source	pH Pu samples	flow rate	colloids	Pu (Bq/L)
Nevada Test Site <sup>a</sup>	Pahute Mesa saturated zone	fractured volcanic tuff	groundwater downgradient well, sodium bicarbonate, low ionic strength	>1 km	low organic content, ~0.15–0.5 <sup>b</sup>	~8	~8	~80 m/year	clays, zeolites, and cristobalite	$2.3 \times 10^{-2}$ – $4.2 \times 10^{-4}$
Rocky Flats <sup>c</sup>	Rainier Mesa vadose zone	zeolitized fractured volcanic tuff	perched water, tunnel seeps, sodium bicarbonate, low ionic strength	~10–100m	15–19	~8	~8		clays and zeolites	$2.0 \times 10^{-4}$ – $3.3 \times 10^{-4}$
Mayak <sup>e</sup>	surface soils <sup>d</sup>	surface soil and surface water	surface waters and shallow streams	10–100m	4–14	~7–10	~7–10	storm runoff and wind	clays and organic	$7.7 \times 10^{-3}$ – $2.8 \times 10^{-4}$
	Lake Karachi	fractured basaltic meta volcanics	groundwater, downgradient well	~4 km	high at source	~7.9–9.3 weakly brine alkaline NaNO <sub>3</sub> solutions	6–8		iron hydroxide, clays, calcite, hematite, and trace silicates	$1.6 \times 10^{-1}$ – $2.9 \times 10^{-2}$
Hanford <sup>f</sup>	100 Area vadose zone	silty sand, sandy gravels	groundwater, downgradient well, slightly alkaline calcium bicarbonate waters	~25m vertical		~7–8	~7–8	0.01–0.24 m/day		$3.7 \times 10^{-6}$ to ND Bq/kg
	200 Area Z-plant vadose zone	unconsolidated fluvial and lacustrine deposits	vadose zone soils 25 m below the Z-plant	20–25m vertical depth		~1–2	6–7 pore fluids	vadose zone	sediments consisting of quartz, feldspar, clay, and trace silicates	

<sup>a</sup>Data from Kersting and Zavarin. <sup>40</sup> Deep groundwater in Pahute Mesa is more similar to Yucca Mountain groundwater: 0.15–0.5 mg of C/L. <sup>118</sup> <sup>c</sup>Data from Santschi et al. <sup>23</sup> <sup>d</sup>Surface springs measured at 0.2 mg of C/L. <sup>91</sup> <sup>e</sup>Data from Navikov et al. <sup>25</sup> <sup>f</sup>Data from Dai et al., <sup>113</sup> Cantrell, <sup>112</sup> and Felmy et al. <sup>111</sup> ND = nondetected.

reduced at high pH (formation of HA–metal complexes).<sup>85</sup> Similar results were also observed with Pu in the presence of kaolinite.<sup>65</sup> These results, together with studies of other radionuclides,<sup>62</sup> suggest that this is an important area of research for understanding the complexity inherent in natural systems.

### ■ INTRINSIC COLLOIDS $\text{PuO}_{2+x}(\text{AM, HYD})$

At high concentrations, Pu(IV) can precipitate to form its own intrinsic colloids (e.g., Eigen colloid, polymer),  $\text{PuO}_2$ .<sup>58,86</sup> These slightly crystalline colloids are not well-defined, and their formation, stability, and structure are not well determined.<sup>58,87</sup> The Pu(IV) intrinsic colloids can form when the concentration of the actinide ions in solution exceeds the solubility of the product for the formation of a solid phase and have been shown to remain quite stable at near-neutral pH.<sup>58</sup> If the initial concentration is high enough to form intrinsic colloids, then transport of stable intrinsic colloids could occur independent of sorption/desorption to other mineral colloids. The concentration of intrinsic colloids in solution could be significantly higher than the calculated thermodynamic solubility of crystalline  $\text{PuO}_2$  in solution, leading to enhanced transport. Elevated concentrations of Pu would be expected at the source of highly contaminated sites, or in the near field of a high-level waste repository, when the engineered containment system is eventually breached. Knowledge of the stability of intrinsic Pu colloids from the near to far field is needed to determine their importance in Pu transport.

Intrinsic Pu(IV) colloids ( $\text{PuO}_2$ ) form 2–5 nm nanocolloids<sup>56,76,88,89</sup> and remain stable in near-neutral solutions.<sup>55</sup> Haire and Lloyd<sup>90</sup> showed that the degree of crystallinity of these nanocolloids could be increased with time but that the size was not significantly affected. Powell and co-workers showed that the 2–5 nm intrinsic plutonium oxide colloids were crystalline at pH 8, not polymers, and easily aggregated into mats of individual 2–5 nm colloids (Figure 5).<sup>89</sup> Figure 5 shows transmission electron microscopy (TEM) images of a mat of 2–5 nm intrinsic colloids (Figure 5A) and a high-resolution TEM (HRTEM) image of individual intrinsic Pu colloids with crystalline structure (Figure 5B). The nanocolloids have a  $\text{PuO}_2$  face-centered-cubic (fcc) structure (Figure 5E) and once formed do not readily sorb to inorganic minerals, even in the presence of minerals with highly reactive surfaces, such as goethite ( $\text{FeOOH}$ ).<sup>89</sup> The well-ordered Pu nanoclusters identified by Soderholm and colleagues were similar (2–5 nm) to the nanocolloids observed by others. These nanocolloids were well-defined crystalline  $\text{PuO}_2$  structures that were stable in high-ionic-strength solutions.<sup>56</sup>

Whether or not intrinsic Pu nanocolloids remain stable as groundwater chemistry and temperatures change remains unknown and is an active area of research. In the laboratory, intrinsic colloids can be synthesized by neutralizing acidic Pu(IV) solutions and can remain stable for significant periods of time.<sup>47,58</sup> To simulate the possible behavior of these colloids under environmental conditions, Zhao and colleagues<sup>91</sup> recently looked at the stability of freshly precipitated intrinsic Pu nanocolloids in the presence of montmorillonite at 25 and 80 °C. Their experiments showed that intrinsic Pu nanocolloids dissolved and sorbed to montmorillonite colloids within days when the overall concentration of Pu dropped below the solubility limit of  $\text{PuO}_{2+x}(\text{s,hyd})$  at pH 8. This study would suggest that these intrinsic colloids are not stable in the presence of montmorillonite and readily dissolve as the Pu

concentration drops below  $\text{PuO}_{2+x}(\text{s,hyd})$  solubility. These results further suggest that, under the conditions studied, intrinsic colloids may not be the dominant species in the far field, where concentrations of Pu are generally well below solubility.

In studying the structure of intrinsic Pu nanocolloids, Powell and co-workers showed that Pu nanocolloids grown on goethite from aqueous Pu(IV) monomers underwent an epitaxial lattice distortion to body-centered-cubic  $\text{Pu}_4\text{O}_7$ . The distortion was not observed when intrinsic Pu nanocolloids were grown on quartz. One important implication of this distortion is that it may lead to a stronger binding of Pu compared to other minerals.<sup>89</sup> This epitaxial distortion was also shown to occur for Pu(IV) on goethite at elevated temperatures (80 °C).<sup>76</sup> Over long experimental time frames (103 days) at both 25 and 80 °C, the distorted Pu nanocolloids remained stable, and there was no indication that the  $\text{Pu}_4\text{O}_7$  nanocolloid had altered to the intrinsic  $\text{PuO}_2$  colloid structure. It is not yet known if this structural distortion occurs on other minerals at elevated Pu concentrations.

For high-level waste repositories, alteration of the engineered barrier materials as well as degradation of the waste form may produce mineral or organic colloids very different from those observed in the natural environment. Buck and Bates conducted a series of hydrothermal experiments investigating the colloid formation of altered borosilicate nuclear waste glass.<sup>92</sup> Using TEM, they identified secondary smectite, phosphate, and carbonate colloids on the surface of hydrothermally altered glass. In a later study using spent nuclear fuel, they showed that a cryptocrystalline Pu-rich layer formed on the altered surface of the spent nuclear fuel, suggesting that intrinsic colloids could be generated and available for transport.<sup>93</sup> These studies point out the need for additional studies to better understand the generation, stability, and mobility of intrinsic Pu colloids under conditions expected at high-level waste repositories.

Experimental efforts on intrinsic colloids, pseudocolloids, and multicomponent systems have shed light on the possible geochemical processes that may be controlling Pu transport. Yet scaling laboratory results on simple systems to more complex field environments has not always reliably predicted environmental behavior. Much more needs to be understood about how Pu behaves in complex, multicomponent systems where the geochemistry along the flow path changes. Field studies can help constrain the behavior of Pu in highly complex systems, and the combination of field studies and laboratory experiments can serve to test conceptual models and improve our ability to understand Pu transport.

### ■ FIELD STUDIES OF PU IN THE ENVIRONMENT

This section summarizes selected recent field studies of Pu transport. The sites chosen are not a comprehensive list but instead are examples where Pu was released to the subsurface under a range of different chemical compositions and biogeochemical depositional environments. The four sites are (1) the Nevada Test Site (Nevada), (2) Rocky Flats (Colorado), (3) Mayak Production Facility (Russia), and (4) Hanford Site (Washington). Table 1 summarizes some of the biogeochemical parameters of each contaminated site.

**Pu Transport at the Nevada Test Site (NTS).** The former NTS, currently called the Nevada National Security Site, was the location of 828 underground and 100 atmospheric nuclear tests conducted between 1956 and 1992 as part of the U.S.



nuclear testing program.<sup>94</sup> Approximately  $4.8 \times 10^{18}$  Bq ( $1.3 \times 10^8$  Ci, decay corrected to 1992) of radioactivity remains in the subsurface, consisting of fission products, activation products, actinides, and tritium.<sup>94,95</sup> Approximately  $3.1 \times 10^{16}$  Bq ( $8.3 \times 10^5$  Ci) of radioactivity comes from Pu.<sup>94</sup> Greater than 95% of the residual Pu and other refractory radionuclides are sequestered in the melt glass that coalesces at the bottom of the cavity.<sup>96,40</sup> As the glass alters, radionuclides are released and are potentially available for transport. For more information on the phenomenology of underground nuclear tests, see work by Kersting and Zavarin and references cited therein.<sup>40</sup>

The NTS is located in an arid desert environment with the majority of the nuclear tests detonated in alluvium or rhyolitic volcanic rock. Approximately one-third of the underground nuclear tests were detonated below the groundwater table, in rhyolitic tuff. The groundwater is deep, roughly more than 250 m bgs, and is predominantly sodium bicarbonate, low ionic strength, and low organic carbon with a pH of  $\sim 8$ .<sup>97,98</sup> In the regions where groundwater flows through fractured volcanic rock, flow rates have been measured up to 80 m/year, whereas in the alluvial basins, groundwater flow rates are much slower, as low as 0.3 m/year.<sup>99</sup>

In the 1980s, Buddemeier and Hunt showed that the refractory radionuclides cerium and europium detected in contaminated deep groundwater at the NTS were associated with the colloidal fraction of groundwater.<sup>100</sup> In a later field study, Kersting and colleagues measured low levels of Pu ( $2.3 \times 10^{-2}$  Bq) associated with the colloidal fraction of groundwater, 1.3 km downgradient from the original Pu source.<sup>22</sup> By uniquely matching the isotopic signatures of Pu in groundwater to an upgradient nuclear test, they were able to show for the first time that Pu associated with the colloidal fraction of groundwater was transported over 1 km. The majority of the colloidal fraction consisted of clays and zeolites. Since then, Pu was detected in groundwater from nine additional well locations. In all cases, greater than 90% of the Pu was associated with the inorganic colloidal fraction comprised of clays and zeolites.<sup>40</sup> These studies showed that low levels of Pu could be transported significant distances ( $>1$  km) in fractured rocks where groundwater flow rates are high and the composition is a near-neutral pH, low-ionic-strength solution.

In the tunnel system of Rainier Mesa, one of the major test areas at the NTS, perched vadose zone waters are characterized by high concentrations of DOM resulting from anthropogenic activities associated with tunnel construction for nuclear testing. A total of 62 nuclear tests were detonated in the vadose zone in the zeolitized fractured volcanic tuff in Rainier Mesa.<sup>101</sup> Water samples had a measured DOM as high as 15–19 mg of C/L compared to the local spring water of 0.2 mg of C/L.<sup>91</sup> Pu concentrations measured in tunnel water ranged from 2 to  $3.3 \times 10^{-4}$  Bq/L (from 54 to  $9.0 \times 10^{-3}$  pCi/L), concentrations higher than those detected in other contaminated water samples at the NTS. Less than 10% of the Pu detected in the vadose zone water was associated with the inorganic minerals (1000–20 nm), which contrasts with what has been observed in the other groundwater samples at the NTS.<sup>91</sup> The inorganic colloids in the Rainier Mesa waters consisted of clays and zeolites. Batch-sorption experiments using Pu in contact with crushed Rainier Mesa volcanic rock were carried out to test the effect of DOM on the Pu solubility. The Pu sorption Kds were up to 2 orders of magnitude lower in water with high DOM compared to the same water with DOM removed or in naturally low DOM groundwater.<sup>91</sup> These results suggest that

Pu-DOM complexes can increase the dissolved Pu fraction, resulting in increased mobility and transport. No further characterization of the  $<20$  nm fraction was undertaken. Under the high organic groundwater conditions at Rainier Mesa, Pu was transported with the DOM and not with the inorganic colloidal fraction of groundwater.

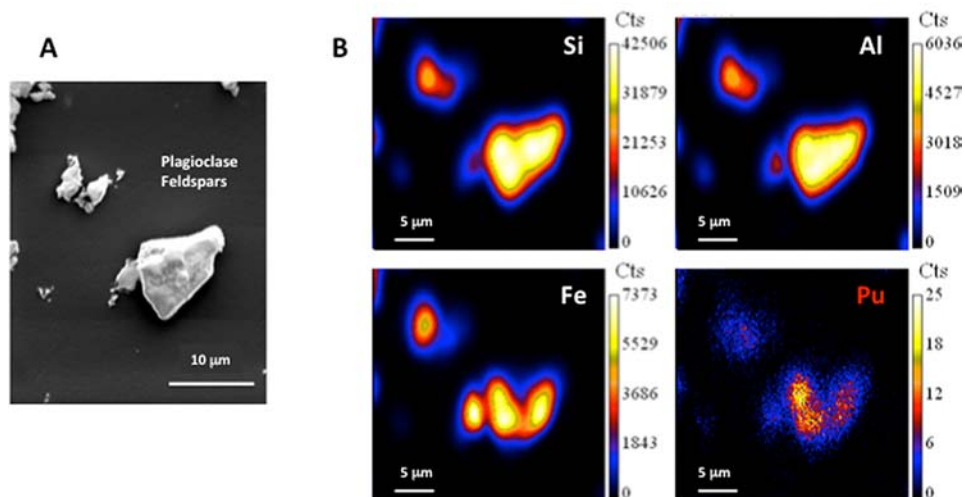
**Pu Transport at the Rocky Flats Environmental Technology Site.** The Rocky Flats Nuclear Weapons Plant (currently the Rocky Flats Environmental Technology Site) was established in 1951. From 1952 to 1989, the plant produced more than 100 t of Pu to manufacture U and Pu components for nuclear weapons.<sup>102</sup> The plant was shut down in 1989, leaving behind a legacy of Pu- and U-contaminated surface water, shallow groundwater, and soil. From 1958 to 1968, leakage of drums that contained Pu-contaminated waste oil in the 903 Pad Storage Area led to releases of Pu to the environment. Contaminated soil was subsequently transported by wind, affecting a much larger area of Rocky Flats than the original 903 Pad Storage. Analysis of the colloidal fraction of the soil by extended X-ray absorption near-edge spectroscopy showed that Pu was in the highly insoluble species  $\text{PuO}_2$ .<sup>103,104</sup>

Rocky Flats is located in the semiarid grasslands on the high plains of Colorado at the eastern edge of the Rocky Mountains. There are two distinct groundwater regimes at Rocky Flats. There is a deep groundwater, about 200–300 m bgs, which is isolated from the shallow groundwater. The shallow groundwater and surface water are inextricably linked because stream channels recharge the shallow groundwater while seeps discharge shallow groundwater to the surface.<sup>102</sup> The shallow groundwater has a pH that ranges between 7.5 and 9.9 and a DOM concentration between 3.6 and 14.0 mg of C/L. Concentrations of Pu in the surface waters ranged from  $7.8 \times 10^{-3}$  to  $2.2 \times 10^{-3}$  Bq/L (from 0.21 to 0.06 pCi/L).<sup>23</sup>

In an initial study by Harnish and colleagues, Pu was detected in shallow surface water samples and associated with the colloidal fraction of groundwater.<sup>105</sup> More recently, Santschi and colleagues showed that greater than 90% of the Pu that was transported with surface waters was associated with nanoorganic ligand complexes (macromolecule,  $>6$  kDa,  $\sim >1$  nm) and not inorganic colloids or inorganic colloids coated by organic matter.<sup>23,24</sup> These studies confirm that, at Rocky Flats, Pu has been transported by organic nanocolloids or macromolecules and not with inorganic mineral colloids.

**Pu Transport at the Mayak Production Association, Russia.** The Mayak Production Association, located near the southern Ural Mountains in Russia, was built in 1948 to produce Pu for nuclear weapons. It consisted of five nuclear reactors and a reprocessing plant. The Mayak region has been severely contaminated due to both routine and accidental releases of radioactivity.<sup>106</sup> From 1949 to 1956, approximately 106 PBq ( $2.9 \times 10^6$  Ci) of nuclear liquid waste was intentionally discharged into the Techa River. Some of the more mobile radionuclides, such as  $^{90}\text{Sr}$ , have been detected more than 2000 km downstream.<sup>106</sup>

Starting around 1951, waste effluent was discharged into nearby Lake Karachai. This lake, which has no outlets, was originally an upland marsh with high organic content.<sup>107</sup> It is underlain by fractured andesitic to basaltic metavolcanics. The discharge waste effluents were weakly alkaline  $\text{NaNO}_3$  brine solutions with a pH between 7.9 and 9.3. Approximately 4440 PBq ( $1.2 \times 10^8$  Ci) of nuclear waste effluent containing  $^{90}\text{Sr}$ ,  $^{137}\text{Cs}$ ,  $^{239}\text{Pu}$ , and  $^{241}\text{Am}$  was discharged into Lake Karachai.<sup>106</sup> Concentrations of Pu in the waste effluent at Lake Karachai



**Figure 6.** NanoSIMS image of sediment grains from the BHK15 sediment sample collected  $\sim 19.5$  m bgs beneath the Z-9 crib in the 200 Area at Hanford, WA. (A) SEM image showing plagioclase feldspar grains Fe with coatings. (B) NanoSIMS elemental analysis showing Si-30, Al-27, Fe-57, and Pu-239 counts for the grains imaged. Pu is strongly correlated with the feldspar grains and other elements in the sediment grains. The Fe coating detected on the feldspar grains was also found on the majority of the grains analyzed. Data were from Kips et al.<sup>116</sup>

were approximately 1000 Bq/L ( $2.7 \times 10^4$  pCi/L). The Pu concentrations measured in groundwater collected from downgradient wells were 4.8 Bq/L at 0.5 km and 0.029 Bq/L ( $7.8 \times 10^{-1}$  pCi/L) at 4.0 km distance.<sup>25</sup>

Novikov and co-workers showed that greater than 90% of the Pu detected 4 km from Lake Karachai was associated with the colloidal fraction of groundwater. They were also able to show that the Pu was associated with iron oxyhydroxide colloids. Particle-size analysis of these colloids demonstrated that between 70 and 90% of the Pu detected in the colloidal fraction was associated with the smallest size 3–10 kD filter ( $\sim 1$ –15 nm). In the near field, the concentration of Pu both at Lake Karachai and in groundwater samples from the nearest wells exceeds the solubility of  $\text{PuO}_{2+x}(\text{s,hyd})$ , favoring the formation of intrinsic Pu colloids. Understanding the processes controlling Pu transport from complex initial source chemistry to more than 4 km downgradient has yet to be fully determined;<sup>108</sup> nevertheless, it is clear that the extraordinarily high levels of radioactivity released over a period of decades has resulted in one of the most contaminated environmental sites in the world. Within this environment, Pu along with other radionuclides has been transported with inorganic iron colloids significant distances through the fractured metavolcanic subsurface geology.

**Pu Transport at the Hanford Site.** The Hanford Site was established in 1943 as part of the U.S. weapons program to produce Pu for nuclear weapons. Located in the semiarid, south-central Washington State, the Hanford Site is located on a sequence of unconsolidated fluvial and lacustrine deposits (sand, gravel, and silt) approximately 30–122 m thick. The sediments overlie the Columbia River basalt, and the water table is variable but estimated between 230 and 270 m bgs in the central areas.<sup>109</sup>

The Hanford Site produced about 67 t of Pu for use in nuclear weapons and was the site of the first nuclear reactor.<sup>110</sup> Separating Pu produced from the reactors and reprocessing the waste resulted in the discharge of large quantities of Pu and other actinides to the shallow subsurface.<sup>111</sup> Releases of radionuclides and hazardous chemicals occurred in a variety of different forms: solid waste in unlined and lined trenches,

liquid waste in shallowly buried tanks, and accidental surface releases. The chemical composition of the waste was highly variable with extremes in the pH, salinity, radionuclide composition, and concentration. Approximately  $2.4 \times 10^8$ – $0.8 \times 10^8$  GBq ( $6.5 \times 10^6$ – $0.22 \times 10^6$  Ci) of high-level waste was discharged to the vadose zone from planned and unplanned releases and leaking tanks, and of this, approximately  $4.4 \times 10^5$  GBq ( $1.2 \times 10^4$  Ci) of  $^{239}\text{Pu}$  was disposed of as liquid waste in the near surface.<sup>111,112</sup> Pu was discharged to the shallow subsurface in over 80 separate locations, although the vast majority of the transuranics was disposed of in the central plateau (200 Area).

Understanding if and when Pu migrates at the Hanford Site is challenging because Pu and other transuranics were released in a wide range of chemical forms, volumes and geologic environments. In some cases, Pu has migrated deep into the vadose zone in significant quantities and yet; at other contaminated locations, Pu and other transuranics have yet to be detected in significant quantities in any groundwater samples.<sup>112,113</sup> A comprehensive review of the contamination from the various locations at Hanford can be found in work by Cantrell.<sup>112</sup>

Dai and colleagues used low-flow pumping techniques to examine the potential for Pu transport in several shallow groundwater wells near known Pu releases in the 100K Area.<sup>113</sup> Contamination was released into the vadose zone comprised mainly of sands and gravelly sands.<sup>114</sup> The groundwater, located about 25 m bgs, is a slightly alkaline, calcium bicarbonate water with a pH between 7 and 8.<sup>114</sup> Several wells did not contain any measurable Pu and the other wells had very low concentrations ( $3.7 \times 10^{-6}$  Bq/kg), concluding that the known Pu inventory previously released to the vadose zone nearby has yet to reach the groundwater in appreciable quantities.<sup>113</sup> In addition, only 7–29% of the Pu detected in the shallow groundwater was associated with the colloidal fraction (1 kDa, 200 nm), much lower than that in the groundwater at the NTS, Rocky Flats, or Mayak.

In contrast to the behavior of Pu in the 100K Area, significant quantities of Pu have migrated vertically in the vadose zone of the Central Plateau (200 Area) largely

associated with the activities at the Z-Plant (Plutonium Finishing Plant) complex.<sup>111</sup> The 216-Z-9 trench was a covered, below-grade, unlined trench that received reprocessed waste from PUREX-type solvent extraction processes with tributyl phosphate (TBP) and carbon tetrachloride organic compounds.<sup>112</sup> An estimated  $4 \times 10^6$  L of acidic (pH  $\sim 2$ ) reprocessed waste was deposited in the Z-9 trench between 1955 and 1962; approximately  $8 \times 10^4$  GBq (2180 Ci) was  $^{239}\text{Pu}$  and  $^{240}\text{Pu}$ . After removal of the  $\sim 0.3$  m of top soil in the 1970s, it is estimated that 38–48 kg of Pu still remains in the soil beneath the trench.<sup>112</sup>

Core samples collected below the Z-9 trench show that large quantities of Pu and Am have migrated vertically within the vadose zone to a depth of  $\sim 36$  m.<sup>111,112</sup> In addition to the actinides, traces of the organic solvent TBP were also detected in some of the deep soil samples, suggesting that the original organic waste solutions have comigrated with the Pu. In the 1970s, crystalline  $\text{PuO}_2$  was detected in the trench sediments, while analysis of the shallow cores showed that the acidic waste had caused extended chemical dissolution of the soil.<sup>115</sup> More recent analysis of these sediments using X-ray adsorption fine structure analysis reconfirmed the presence of intrinsic  $\text{PuO}_2$ .<sup>111</sup> However, analysis of Pu in the deeper samples (20–22 m bgs) is less straightforward, with Pu–O bond lengths suggesting that Pu may not be present in the  $\text{PuO}_2$  form.<sup>111</sup>

Two sediment samples from 20 and 25 m bgs at the Z-9 trench were analyzed using a nanoscale secondary-ion mass spectrometer (NanoSIMS) in an effort to detect and image Pu and determine its association with the sediments.<sup>116</sup> The Pu measured in the soil samples was  $\sim 77.1$  Bq/g ( $\sim 2.1$  nCi/g). The NanoSIMS has high spatial resolution (50–100 nm) and sensitivity concomitant with the mass specificity. The primary ion beam rasters the sample to image and analyzes quantitatively the composition and isotopic ratio of the samples.<sup>117</sup> In this study, Pu was found on several different primary silicate and oxide minerals (e.g., quartz, feldspar, biotite, and clay). The Pu was associated with minerals that ranged from less than  $1 \mu\text{m}$  (colloidal) to tens of micrometers in diameter. Figure 6 shows Pu detected on several primary feldspar grains. The Pu is colocalized with Si, Al, and Fe. The Fe is an iron oxide surface coating observed on many of the sediments. Many of the mineral grains that are associated with the Pu are too large to have migrated through the vadose zone. It is more likely that the organic TBP and  $\text{CCl}_4$  solution played a significant role in facilitating the vertical transport of Pu. Beneath the Z-9 trench, it does not appear that Pu sorbed to inorganic colloids facilitated the vertical transport of Pu.

The four field locations highlighted in this review provide evidence that Pu has migrated significant distances in the subsurface. Yet, the biogeochemical conditions facilitating its transport are not necessarily the same at each location (Table 1). At both the NTS and Mayak Site, where you have groundwater flowing through fractured volcanic rocks at near-neutral pH, inorganic colloids were shown to facilitate the transport of Pu over large distances ( $>1$  km). Despite inorganic colloids being involved in facilitating Pu transport at both NTS and Mayak, each has a very different source chemistry and the biogeochemical transport pathway from the source to distal wells is not well understood. In Rainier Mesa, the NTS tunnel system, and Rocky Flats, where contaminated water has a high organic content, the Pu was overwhelmingly associated with the organic fraction ( $<20$  nm) of the groundwater and not with

inorganic colloids. At Hanford, Pu was detected as a surface coating on multiple primary minerals in vadose zone sediments 25 m vertically beneath a liquid waste disposal crib. It appears that the large volumes of highly acidic organic waste solutions deposited at the surface transported the Pu vertically. At a second Hanford location, closer to the Columbia river (100K Area), samples from wells downgradient of known contaminant spills had trace to nondetectable levels of Pu in the groundwater, suggesting that there are conditions where Pu transport appears to be minimized. Collectively, knowledge gained from studies undertaken at these four field sites has shown that Pu has migrated and that variations in the local geology, geochemical conditions, colloidal composition, and difference in the initial source characteristics are profoundly important in controlling transport.

## ■ SUMMARY AND CONCLUSIONS

The last 2 decades have seen a tremendous increase in our understanding of the chemical behavior of Pu and other actinides in the environment, yet we are still not at a level of understanding that permits us to predict the behavior of Pu for a range of hydrogeologic environments. It is clear from recent laboratory and field studies that long-distance transport of Pu can and does occur and that there is not one process or mechanism to explain the body of experimental and field evidence. Results from the few selected field studies discussed above show that Pu can migrate by several different processes: associated with inorganic colloids, associated with small organic nanocolloids, and with organic solvents from initial acidic waste solutions not associated with inorganic colloids. Equally important is the need to understand the observation at the 100 K area at Hanford, where Pu was detected very low abundance and not strongly associated with the colloidal fraction appreciable into a porous media vadose zone setting. Collectively, knowledge gained from studies undertaken at these four field sites suggests that Pu has migrated and that variations in the local geology, geochemical conditions, colloidal composition, and differences in the initial source characteristics are profoundly important in controlling its transport.

The laboratory and field research on the chemical behavior of Pu in the environment summarized in this review provides an important foundation for additional studies needed to determine the dominant biogeochemical processes that enhance or inhibit the cycling and mobility of Pu in the subsurface. Future research directions should focus on (1) better understanding of the molecular level processes that control Pu sorption/desorption reactions with inorganic, organic, and microbial surfaces, (2) investigating the behavior of Pu in more complex multicomponent systems where microbial, organic matter, and inorganic colloids coexist, (3) investigating the formation and stability of intrinsic Pu colloids as a function of temperature and multicomponent system chemistry, (4) studying field-scale transport where the source term is known under a range of various colloidal and hydrogeologic conditions, especially in vadose zone settings, (5) investigating the chemical conditions where intrinsic and pseudocolloids are not stable, thereby minimizing colloid-facilitated transport, (6) developing reactive transport models that can incorporate the molecular-level geochemical processes that scale up to kilometer-range transport, and (7) continuing to develop a robust conceptual model of Pu mobility and



immobility that can be tested by future experiments, field studies, and transport models.

The current lack of an integrated strategy for the safe disposal of nuclear waste still remains one of the most urgent environmental problems today. The current demand for nuclear energy coupled with the existing legacy of waste from the nuclear fuel cycle requires a continued effort to develop a credible strategy for isolating, storing, and preventing the release of long-lived, highly toxic actinides such as Pu. Without a better mechanistic understanding of the biogeochemical processes that both facilitate and limit Pu transport, advancements needed for the development of reliable transport models will remain limited. Despite the scientific challenges this problem poses, tremendous progress and new insights have been made. Recent advances by the scientific community provide a strong framework for moving forward and, coupled with new technology, will help scientists understand and predict how Pu can and cannot migrate, ultimately leading to safe storage strategies for high-level waste repositories.

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### Notes

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