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The Role of Colloids in the Transport of Plutonium and Americium: Implications for Rocky Flats Environmental Technology Site

A.B. Kersting

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The Role of Colloids in the Transport of Plutonium and Americium: Implications for Rocky Flats Environmental Technology Site

By
Annie B. Kersting

Abstract.   Colloids are small particulates (ranging in size from 1 to 0.001 micron) composed of inorganic and organic material and found in all natural water. Due to their small size, they have the ability to remain suspended in water and transported. Small amounts of plutonium (Pu) and americium (Am) can adsorb (attach) to colloids, and/or form colloidal-sized polymers and migrate in water. At Rocky Flats Environmental Technology Site (RFETS) sedimentation and resuspension of particulates and colloids in surface waters represent the dominant process for Pu and Am migration. The amount of Pu and Am that can be transported at RFETS has been quantified in the Pathway Analysis Report[1]. The Pathway Analysis Report shows that the two dominant pathways for Pu and Am transport at RFETS are air and surface water. Shallow groundwater and biological pathways are minor.

Introduction.   A dominant, and often controlling feature of Pu and Am geochemistry is their very low solubility in natural waters, and their strong tendency to adsorb to soil and mineral surfaces. Based on these geochemical characteristics, one might conclude that low solubility radionuclides like Pu and Am would adhere to the geological matrix, and would remain immobile in the environment. Yet, there have been a growing number of field studies documenting movement of low concentrations of low-solubility radionuclides in surface and groundwater[2-4]. A consensus as to the mechanisms responsible for the apparent observations has been slow to emerge. In part, the natural complexity of geologic environments has made conclusions regarding transport sometimes difficult. In addition, radionuclide concentrations in the field are generally very low, and many times the levels are near the detection limit of the instrumentation used, resulting in ambiguous interpretations. Reconciliation between processes that occur in the laboratory at high radionuclide concentrations and those in the field at much lower concentrations are sometimes difficult. These issues, in part, have lead to a previous lack of agreement between field, laboratory and modeling studies.

One explanation that has recently gained support is that small concentrations of low-solubility radionuclides, such as Pu and Am can be transported in groundwater either by "hitching a ride" on naturally occurring colloids (sometimes called pseudocolloids) or are themselves colloidal size polymers (intrinsic colloids) (Figure 1). Colloids are naturally occurring small particulates usually defined with a diameter between 1 nm and $1\mu m$[5,6] and due to their small size, have the ability to remain suspended in water and transported.
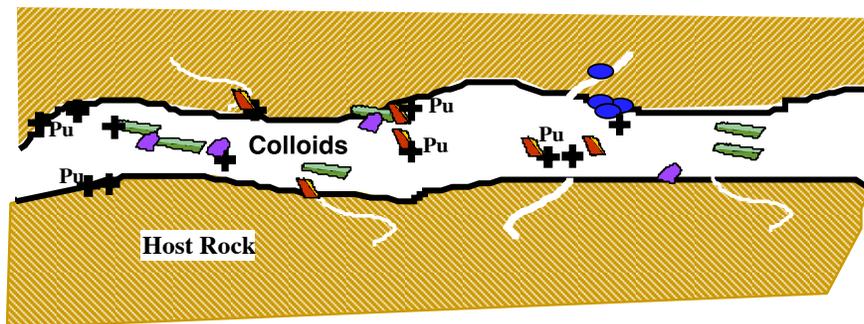
Figure 1   Cartoon drawing of colloids moving in groundwater through a fractured rock. The cartoon represents several possible scenarios for Pu. In this cartoon, Pu (shown as a cross,+) is drawn: 1) attached to the fracture walls (immobile), 2) sorbed to different minerals (shown by different shapes) (mobile), 3) sorbed to minerals that are attached to the fracture walls (immobile), and 4) by itself as a polymer or intrinsic colloid (mobile).

Although the idea that colloids may facilitate the transport of contaminants in groundwater is not new,[7] compelling field evidence has previously been lacking. In addition, new techniques have allowed for more detailed investigations, and such studies have provided better insights into the physicochemical nature of colloid and particulate transport. In order for the mechanism of colloidal transport (pseudo or intrinsic) of low-solubility radionuclides to occur, colloids must exist and be stable, radionuclides must have a high sorption affinity for the colloids (in the case of pseudocolloids), and the hydrologic conditions must be conducive for colloid transport[8]. The contaminant source, and the concentration and size of colloids determine the amount of contamination that can be transported in water. If the concentration of colloids in water is low, or water sparse, then the process of colloid-facilitated contaminant transport becomes unimportant as only a small amount of contamination can migrate. If there is not enough water to transport colloids through a given geologic medium (e.g. soil, fracture rock) then colloid-facilitated transport cannot occur. In the following sections, our current understanding of colloid facilitated transport of low-solubility radionuclides will be summarized and its relevance discussed for RFETS.

What are Colloids? Colloids are small, naturally occurring particulates that are ubiquitous in groundwater, and composed of inorganic minerals or organic species (Figure 2). Groundwater colloids originate from mechanical weathering of rocks, plants and soil[9]. The inorganic mineral composition of the colloids is reflective of the host rock mineralogy or the fracture-lining minerals, and consists of common alteration minerals such as, clays, zeolites, Fe-oxides, Mn-oxides, and silica[3,10-12]. Organic colloids are common in surface and shallow waters. In contrast, the organic content of deep waters in fractured rock is generally low and these systems are dominated by inorganic colloids[13].
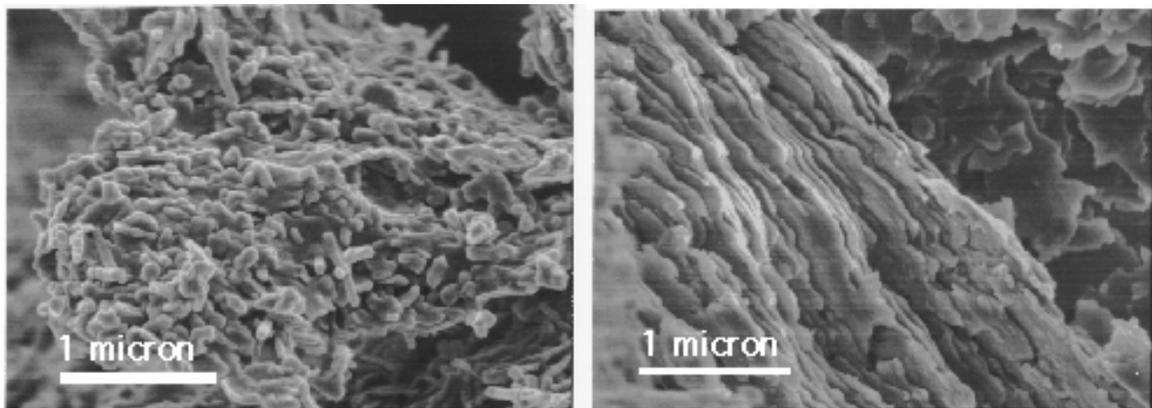
Figure 2. High-resolution scanning electron microscope images of naturally occurring inorganic colloids filtered from groundwater collected at the Nevada Test Site. This sample consists of clays, zeolites and silica minerals. Scale bar is at the bottom left.

In addition to sorbing to inorganic and organic colloids, Pu and Am ions can also form colloid-sized polymers and are sometimes called intrinsic colloids. Intrinsic colloids can form when the concentration of the actinide ions in solution exceeds the solubility product for the formation of a solid phase. The solubility product of an actinide ion is dependent on the oxidation state of the ion and the composition of the groundwater. For example, the intrinsic colloid of Pu(IV) can be easily produced and remain stable in near neutral solutions[14].

Studies have shown that colloids are found in all natural waters, but they have a huge range in concentration. Measured values range from 0.0002 to 200 mg/L, but difficulties in sampling and analysis make accurate concentrations difficult and measured values most likely represent a maximum[9]. The rate at which colloids are transported is a function of both the size and charge of the colloid and the hydrologic conditions of the environment. The amount of contamination available, concentration and composition of the colloids, and local hydrologic conditions of the environment are all important factors in determining how much contamination can be transported via colloids.

Laboratory studies. If Pu has a high sorption affinity for colloids, and is not quickly desorbed, its transport is much more likely. Extensive literature exists from laboratory studies on the sorption/desorption (attachment/detachment) behavior of different low-solubility radionuclides to inorganic and organic colloids[15-18]. Under ambient pH, it has been shown that Pu(IV) and Pu(V) sorb strongly to a variety of common inorganic minerals and organic material.

Laboratory transport experiments were carried out to determine if Pu pseudocolloids injected into fractured volcanic rock cores could be transported[19]. Results from these experiments show that colloids are capable of being transported in a fracture flow, saturated environment, although the Pu concentrations were significantly attenuated during transport. Laboratory transport experiments were also carried out simulating alluvium conditions where groundwater flows in the absence of fractures[20]. Solutions containing Pu, Am, and Np polymer (intrinsic colloids) in solution were passed through crushed volcanic tuff. These studies showed that colloidal transport of Pu(IV) and Am(III) through crushed tuff does occur, but the overwhelming majority of the colloids (>90%) remains on the tuff and is not transported.

Field studies. Laboratory studies have shown that it is possible for the colloidal transport of Pu and Am to occur, although the concentrations of radionuclides are significantly attenuated during transport. Does the mechanism of colloid-facilitated transport occur in nature, in an environment much more complicated than in a laboratory? A pioneering field study was conducted at the Nevada Test Site (NTS) to determine if the radionuclides in groundwater flowing through fractured rock were associated with the colloidal fraction of the groundwater[2]. The NTS is the location of over 800 underground nuclear tests. After detonation of an underground nuclear test, a residual source term of radioactivity remains. Groundwater was pumped and filtered from a well down gradient from an underground nuclear test. Greater than 90% of low-solubility radionuclides, Co, Ce, Eu, were associated with the colloidal fraction of the groundwater. In a more recent study, low levels of Pu, Am, Eu, Co, and Cs were detected in groundwater 1.3 km down gradient of a different nuclear test also hosted in fractured volcanic rock at the NTS[3,21]. Greater than 95% of the Pu was associated with the colloidal fraction of the groundwater. Under the conditions at the NTS, the process of colloid-facilitated transport has resulted in the migration of low-levels of low-solubility radionuclides.

While several recent field studies demonstrate that low levels of Pu can migrate either by adsorbing to colloids or as intrinsic colloids, other field studies suggest that colloids and their sorbed contaminants are not always so easily transported. At a field site in unsaturated alluvium, 1-2 micron styrene microspheres (surrogates for natural colloids) were injected into wells at Lawrence Livermore National Laboratory[22]. No microspheres were detected in any down-gradient receptor wells, suggesting that under the field conditions employed, colloids are not easily transported.

A naturally occurring high-grade uranium ore in Oklo, Gabon reached criticality approximately 2 billion years ago producing several natural fission reactors as a result of highly reducing environmental conditions and the presence of abundant organic material[23]. This unique geologic situation produced several natural fission reactors by thermalized neutron-induced fission of ^{235}U, as well as neutron capture species such as ^{239}Pu from ^{238}U. The fissiogenic daughters and the U, Pu, are retained in the uraninite and secondary (U,Zr) silicate minerals and have not migrated, even after a significant period of time[24].

The field and laboratory studies discussed above highlight the importance of the specific local geologic, geochemical, and hydrological conditions as well as emplacement conditions of actinides in determining if colloids will or will not facilitate the transport of low-solubility radionuclides.

Colloid-facilitated transport of Pu and Am at RFETS   At RFETS, Pu and Am contamination has occurred in the shallow subsurface composed of alluvium (Figure 3). Water at RFETS and the surrounding area moves as surface water, shallow groundwater and deep groundwater[1]. Surface water generally flows west to east. Shallow groundwater refers to water within the alluvium and weathered bedrock geologic units and is found to a depth of 30 meters. Surface water and groundwater are inextricably linked. Water from stream channels infiltrates downward, recharging the shallow groundwater. Beneath the alluvium is a highly, impermeable bedrock that inhibits vertical flow. As a result, shallow groundwater flows laterally where it either discharges as baseflow into the streams or into valley-fill alluvium material. Approximately 200-300 meters below the surface lies the Fox Hills Sandstone, where, isolated from the surface and shallow groundwater, the deep regional groundwater flows. The deep groundwater is not a pathway for actinide contaminants because of its isolation from the surface and shallow groundwater[25].
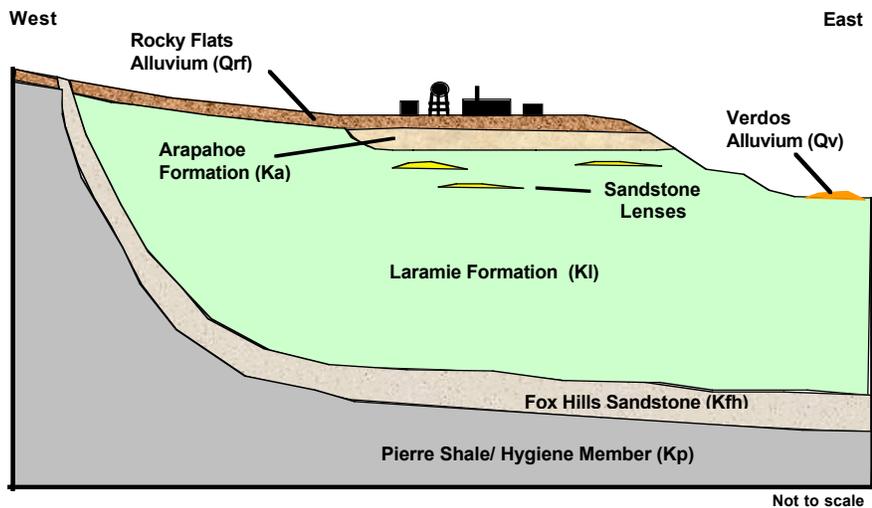

Figure 3.   Schematic cross-section of RFETS, west to east. Regional Fox Hills Sandstone (regional aquifer) is 200-300 meters below the ground surface and isolated from shallow ground water by the impermeable claystone of the Laramie Formation.

Several field studies were undertaken at RFETS to assess the ability of colloids and particulates to transport Pu and Am in the surface and shallow groundwater. Surface water samples were collected from storm runoff and pond discharge between 1998 and 2000[4]. The collected water contained low levels of Pu and Am. Results showed that greater than 90 percent of the Pu and Am was detected in the particulate and colloidal fractions of the groundwater. Isoelectric experiments showed the Pu

was associated with the organic component of the colloids. The low levels of Pu and Am in surface water at RFETS are transported by the colloidal and particulate fraction and not the dissolved fraction of the water.

In an earlier field study conducted in 1984, shallow groundwater from a single well was filtered, and analyzed for radionuclides[26]. Low levels of Pu were associated with the particulate and colloidal fractions. Colloid concentrations were low (<1 mg/L) and consisted predominantly of clays. This study documents that Pu is associated with the colloidal fraction of the groundwater; yet, the low concentration of colloids observed limits the ability of colloids to transport significant quantities of Pu or Am. Caution must be used when interpreting these data as Pu concentrations were near the detection limit and the potential to contaminate the sample due to sampling or well installation could not be eliminated.

In an effort to further evaluate the potential for contaminant transport in the shallow groundwater, a series of shallow wells were drilled, sampled and analyzed for colloids and radionuclides[1]. Special effort was made in the design and sampling of the wells to limit possible down-hole contamination due surface soil interaction. Concentrations of Pu and Am in four shallow groundwater samples were very low but measurable (i.e., ≤ 0.02 pCi/L)[27], consistent with the initial results of Harnish et al., (1984). Although care was taken to prevent surface contaminants from being carried downhole, the possibility cannot be ruled out. The concentrations and corresponding colloid loads are low and do not represent a significant source for transport of low-solubility radionuclides.

Field studies at RFETS have demonstrated that particulate- and colloid-facilitated transport of low-solubility radionuclides, such as Pu and Am, is the dominant mechanism for transport in the surface water and shallow groundwater pathways. The low concentrations of colloids detected in shallow groundwater wells, limits the amount of Pu and Am that can be transported in this pathway. Studies carried out at RFETS have significantly improved our understanding of the *process* by which Pu and Am are transported, and give confidence to the recent pathway analysis that concludes that wind and surface water erosion are the dominant actinide migration pathways at RFETS[1] (Figure 4). Unlike other geologic environments, deep groundwater at RFETS is effectively isolated from shallow and surface water, preventing a pathway for deep vertical transport of Pu and Am.

All Pathways
Estimated Off-Site Annual Actinide Loads
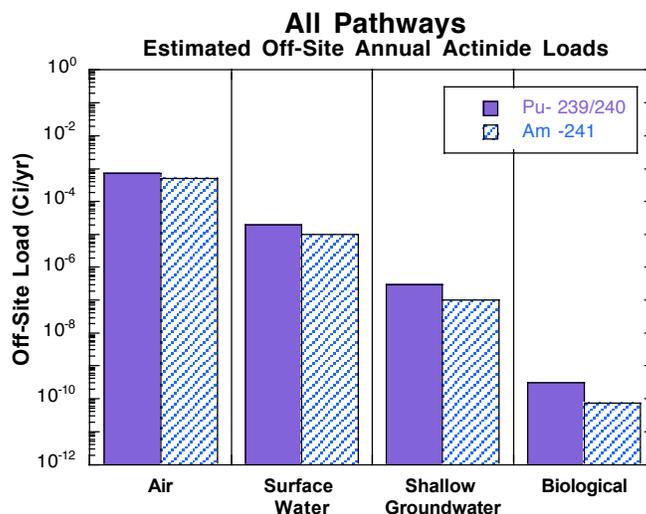
Figure 4.   Comparison of the quantitative estimates of off-site actinide loads from the air, surface water, shallow groundwater and biological pathways. Note log scale. After Kaiser-Hill, (2002).

Summary.   Plutonium and Am migration in the environment can occur because small amounts of these very low-solubility actinides can either attach to particles or colloids (pseudocolloids) or are themselves colloid sized polymers (intrinsic colloids). Pseudocolloids are present in nearly all waters and are formed as a result of the weathering of rocks, soil and plant material. Although the idea that colloids can facilitate the transport of contaminants in groundwater is not new, recent field studies provide compelling evidence that under ambient groundwater conditions, colloid-facilitated transport is the *dominant process* by which low levels of Pu and Am can be transported in the environment.   Advances in technology have allowed for detection of radionuclides at lower concentrations resulting in detailed studies that provide better understanding of this process. At RFETS, sedimentation and resuspension of particulates and colloids in both the surface and shallow groundwater represent the dominant processes for low levels of Pu and Am transport.   Since colloids are a part of the overall particulate spectrum, the amount of Pu and Am that can be transported at RFETS has already been quantified in the Pathway Analysis Report.   The Pathway Analysis Report shows that the two dominant pathways for Pu and Am transport are air and surface water with shallow groundwater and biological transport existing as minor pathways.

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