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Colloid-Facilitated Actinide Transport in a Cementitious-Impacted SRS Groundwater

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EXECUTIVE SUMMARY

The objective of this report is to provide a literature review relevant to the question of whether colloid facilitated transport of plutonium is enhanced in a cementitious groundwater system on the Savannah River Site (SRS). Contaminant transport is commonly described as taking place in a system with a mobile aqueous phase and an immobile solid phase. There has been an increasing awareness of a third phase, a mobile solid phase, also referred to as a mobile colloidal phase. Mobile colloids consist of organic and/or inorganic submicron-particles that move with groundwater flow. When radionuclides are associated with the mobile colloids, the net effect is that radionuclides can move faster through the subsurface system than would be predicted by transport models that do not include mobile colloids. It is important to distinguish between subsurface colloids and subsurface mobile colloids. The subsurface environment includes an enormous reservoir of colloids, but only a tiny fraction, if any, are mobile. Mobile colloid formation is commonly described as involving a three-step process: genesis, stabilization, and transport. It was concluded that there is a strong likelihood that submicron colloids of plutonium exist near the source term, (i.e., the genesis step is likely completed). While such particles have not been directly detected, it is highly likely that plutonium could either attach to submicron particles in the sediment or that submicron plutonium fragments exist at the source. However, the tendency for these plutonium colloids to move in the SRS subsurface is extremely low, especially in engineered cementitious environments where the ionic strength of the solution and the elevated concentrations of divalent cations greatly curtails colloid suspension stability (i.e., the stabilization step is likely not completed). Together these data strongly indicate that plutonium-bearing colloids would likely exist in the near field of a tank closure facility, but the colloids would be unlikely to be mobile, thereby providing a vector for enhanced transport. Under cementitious leachate impacted groundwater conditions, it is reasonable to assume plutonium transport occurs primarily as a two-phase system, a mobile aqueous phase and an immobile solid phase.

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LIST OF ABBREVIATIONS

Am	Americium
DOE	Department of Energy
MCL	Maximum Contaminant Level
PA	Performance Assessment
Pu	Plutonium
SRMC	Savannah River Mission Completion
SRNL	Savannah River National Laboratory
SRS	Savannah River Site

1.0 Introduction

Contaminant transport is traditionally modeled as a two-phase system: a mobile aqueous phase and an immobile solid phase. There has been an increasing awareness of a third phase, a mobile solid phase, or mobile colloidal phase. Mobile colloids consist of organic and/or inorganic submicron-particles that move with groundwater flow. When radionuclides are associated with the mobile colloids, the net effect is that radionuclides can move faster through the subsurface system than would be predicted by transport models that do not include mobile colloids. The earliest reviews of colloid-facilitated transport of contaminants were by McDowell-Boyer et al. (1986) and McCarthy and Degueldre (1993). A review focused on the role of nanoparticle-enhanced contaminant transport was provided by Kretzschmar and Schafer (2006).

2.0 Mobile Colloid Formation

It is important to distinguish between subsurface colloids and subsurface mobile colloids. The subsurface environment includes an enormous reservoir of colloids, but only a tiny fraction, if any, are mobile. Mobile colloid formation is commonly described as involving a three-step process: genesis, stabilization, and transport. Colloid genesis describes how the submicron particles are formed in groundwater. Stabilization describes how the colloids are brought into suspension, which is a function of the colloid and groundwater composition and water flow forces. Transport describes how the suspended colloids move through the porous media or are retained by physical forces (such as diffusion, straining, or gravitational settling) or physicochemical attraction to the porous matrix. If any of these steps is interrupted, then mobile colloids are not formed.

2.1 Genesis of Plutonium-Bearing Colloids

With little uncertainty, Pu that leaves the engineered system and resides in the subsurface environment will be in colloidal form, either as intrinsic colloids (Pu (co)precipitates) and/or Pu pseudo-colloids (Pu bound to minerals). The reason for this is that Pu in the reduced form as Pu(III) or Pu(IV) is sparingly soluble and will precipitate out of solutions, including potentially forming intrinsic colloids. Furthermore, what little dissolved Pu that may be in solution, would have a very strong tendency to bind to SRS sediment surfaces (Kaplan, 2021). Ramsay (1988) presented strong evidence for the existence of colloid particles in glass and cementitious leachate and provided an in-depth review of the various types of colloids that can/may exist (*e.g.,* glass fragments, precipitation products, geological materials, secondary phases formed from glass leachate).

2.2 Colloid Suspension Stabilization

Regarding the second step involving colloid suspension stabilization, colloid dispersion experiments were conducted with SRS sediments in which they varied ionic strength (the amount of salts in solution) and pH, two key factors controlling colloid suspension stabilization (Kaplan, 2006; Kaplan et al., 1996). At background sediment pH values (pH 4.3 to 6.9), there was minimal or no tendency for clays to disperse. This is not surprising because if clays dispersed under background conditions, there would be no clays remaining in soil; they would have been transported away with infiltrating groundwater. As the pH was increased, there was a critical pH value, generally about 0.5 to 1 pH unit greater than background, above which significant dispersion occurred. However, the suspensions at background levels or elevated pH levels, could be readily flocculated by increasing the solution ionic strength to levels that would be readily achievable with cementitious leachate. Cementitious leachate promotes that flocculation of colloids not only due to its elevated ionic strength, but also by its composition of containing more strongly flocculating divalent ions, Ca^{++}, as compared to the SRS groundwater that includes a greater mixture of monovalent cations, Na^+.[1] Together these results indicate that while the cementitious leachate is expected to increase groundwater pH that would lead to greater colloid stability, the ionic strength and divalent nature of the leachate offsets this effect resulting in suspended colloid flocculation.

2.3 Colloid Mobility

In a study designed to evaluate the effect of a high-pH cementitious leachate on colloid mobilization, columns studies were conducted with SRS subsurface sediments (Li et al., 2012). The extreme alkaline pH environments of the cementitious leachate resulted in a sharp spike in leachate turbidity, demonstrating that the leachate temporarily promoted the formation of mobile colloids. The mobile colloids collected in the leachate of the column consisted primarily of goethite, but they were formed only in the alkaline front as it penetrated through the sediment column. Turbidity sharply decreased to negligible levels in a fraction of one pore volume, even though the cementitious-impacted groundwater chemistry did not change. Additional experiments conducted by Li et al. (2012) that evaluated the conditions away from the cementitious source indicated that there were essentially no mobile colloids present. These experiments indicate that SRS soils will disperse at the cementitious leachate front as it enters the subsurface environment but does not maintain a dispersive chemical environment immediately behind the front. In the context of a DOE Performance Assessment (PA) involving a cementitious waste form and/or containment barrier, this cementitious front would start moving into the underlying aquifer early in the life of the dispositioned waste/tank, a time when Pu concentrations would be expected to be at a minimum because the Pu movement would be retarded with respect to the water comprising the leachate solution.

In a second set of column studies, Li et al. (2013) tested whether the presence of organic matter could promote the formation of mobile colloids. They reported that increases in natural organic matter concentrations resulted in a systematic increase in colloid charge and tendency to remain in a stable suspension. However, even when chemical conditions favored colloid dispersion (e.g., elevated pH values or organic matter concentrations) subsequent colloid transport was almost completely eliminated due to the SRS sediments' innate capacity to filter out dispersed colloids from moving freely through the pore spaces. While elevated organic matter concentrations are not expected under disposal conditions, they may provide a conservative estimate of the tendency for colloids to be transported (step 3 in mobile colloid formation) because the presence of organic matter promotes colloid suspension stability (step 2 in mobile colloid formation).

3.0 Field Studies Reported in the Literature

There have been four locations where subsurface colloid facilitated transport has been observed: 1) Pu at the Nevada Test Site (Kersting et al., 1999), 2) Pu and Am at the Los Alamos National Laboratory (Penrose, 1990), 3) Pu at the Mayak Production Association in Russia (Novikov et al., 2006), and 4) Pu and Am in F-Area, SRS (Buesseler et al., 2009; Dai et al., 2002; Kaplan et al., 1994). In each case, the Pu concentrations associated with colloids were several orders of magnitude below drinking water levels, they were highly disturbed systems (pH 3, nuclear bomb test site, nuclear accidents) and none of these cases involved cementitious engineered systems.

Field studies of colloid facilitated transport of Pu have been studied on the SRS by two groups, the University of Georgia and SRNL (Kaplan et al., 1994; Seaman et al., 1995; Seaman et al., 1997)[2] and Woods Hole Oceanographic Institution and SRNL (Buesseler et al., 2009; Dai et al., 2002). Together their results detected the presence of Pu on mobile colloids about 700 m from the source (F-Area Seepage Basin). Kaplan et al. (1994) measured Pu associated with a filterable fraction in groundwater recovered in F-Area, which is <10 miles from the F- and H-Area tank farms. Very low concentrations of Pu were detected in

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[1] According to DLVO theory, the tendency for colloids to flocculate out of suspension is proportional to the square power of the ion charge. For example, it is expected that it would require ¼ ($Z^2 = 2^2$) the concentration of a divalent solution to flocculate mobile colloids out of solutions as compared with a monovalent solution ($Z^2 = 1^2$). This occurs because divalent cations, as compared to monovalent cations, reduce the thickness of the double electric layers (the surface charge) and thus the surface potential of the colloidal particles.

[2] Kaplan et al. (1994) also detected Th, U, Am, Cm and Ra on colloids, and the fraction of radionuclides associated with colloids increased as: Pu > Th > U > Am = Cm > Ra.

association with groundwater colloids, 0.003 pCi/L $^{239/240}$Pu. To put this concentration in perspective, the Maximum Contaminant Level (MCL) for $^{239/240}$Pu is 15 pCi/L (Federal Register, Vol. 65, No. 236, December 2, 2000); thus, the amount found associated with colloids was 5000 time less than the MCL. Furthermore, there was an estimated 7,000,000,000 pCi of $^{239/240}$Pu disposed in the F-Area seepage basins. However, it does demonstrate that Pu-bound to colloids can move considerable distances, much faster than predicted based on conventional two-phase model.

Woods Hole Oceanographic Institution and SRNL returned to F-Area in 2004 to characterize changes in Pu oxidation states and Pu association with colloids in groundwater samples collected six years earlier (Buesseler et al., 2009). They reported small concentrations of Pu associated with colloids. The percentage of Pu associated with colloids, 1 to 23%, was less than that reported by Kaplan et al. (1994), who reported 28 to 100%, but was more than that reported by Dai et al. (2002), 0 to 10%. Buesseler et al. (2009) reported that the fraction of groundwater colloidal Pu increased systematically with decreases in redox conditions. They observed greater dynamic shifts in Pu speciation, colloid association, and transport in groundwater on both seasonal and decadal time scales and over shorter field spatial scales than commonly believed.

4.0 Summary

Colloid facilitated transport of Pu from SRS tanks would first require that the Pu be associated with <1-micron particles. While this has not been directly detected, it is highly likely that Pu could either attach to submicron particles in the sediment or that submicron Pu fragments exist at the source. Depending on its oxidation state, Pu can be either sparingly soluble and strongly binding to sediments (Pu(III) and Pu(IV)), or it could be strongly binding to sediments (Pu(VI) (Kaplan, 2021). However, the tendency for these Pu colloids to move in the SRS subsurface is extremely low, especially in engineered cementitious environments where the ionic strength of the solution and the elevated concentrations of divalent cations greatly curtails colloid suspension stability (Kaplan, 2006; Li et al., 2012). Furthermore, when highly dispersive colloids (organic matter amended colloids) were introduced into SRS sediments, the trapping capacity (interception) of the sediment readily removed the colloids from the mobile phase (Li et al., 2013). Together these data strongly indicate that Pu-bearing colloids would likely exist in the near field of a tank closure facility, but the colloids would be unlikely to be mobile, thereby providing a vector for enhanced transport. Under cementitious leachate impacted groundwater conditions, it is reasonable to assume Pu transport occurs primarily as a two-phase system, a mobile aqueous phase and an immobile solid phase.

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