

## **10 Colloids and the Transport of Radionuclides**

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### **Abstract**

Colloids are small, less than one micron particles found in all natural water. They are composed of inorganic, organic or microbial material and can act as carriers for low-solubility radionuclides. Some actinides can hydrolyze to form an oxide or other pure phases called intrinsic colloids. However, the presence of colloids does not necessarily guarantee the facilitation of the transport of radionuclides. Other factors such as colloid filtration, stability, groundwater flow rate, groundwater chemistry, desorption/dissolution rates of the radionuclides are all important parameters that determine colloid facilitated transport of a specific radionuclide. This chapter focuses on our current progress in understanding the conditions and mechanisms that enhance colloidal transport. Additional emphasis is given to field sites where investigations have shown colloids to facilitate the far-field transport of radionuclides. Understanding the biogeochemical conditions that facilitate the transport of low-solubility radionuclides can help us design high-level waste repositories that minimize these conditions.

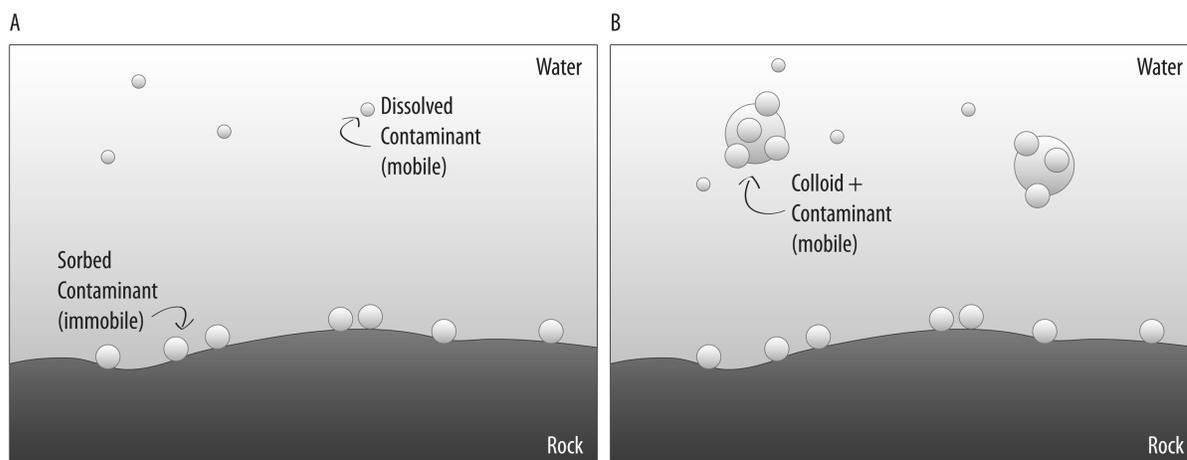
### **10.1 Introduction**

Until the mid 1980's it was thought that the transport of contaminants would only occur when dissolved in a liquid or gas phase. Contaminants that were attached (sorbed) to the soil or rock matrix were considered immobile (Figure 1a). Transport models developed to predict contaminant migration accounted for only two contaminant forms: a dissolved (mobile) phase

or a sorbed/precipitated (immobile) phase. Contaminants that were not very soluble in water or readily sorbed to a solid phase were considered to be largely immobile because they were effectively removed from the mobile phase. Since many radionuclides (e.g. Pu, Am, Eu, Cs, Sr) have very low solubility and/or readily sorb to solid phases it was thought that they would not be transported and as a result, would not contaminate groundwater or be a significant danger to down-gradient receptors. As an increasing number of field studies began to contradict this assumption, it became apparent that the theory suggesting the immobility of strongly sorbing/insoluble contaminants was not consistent with observations. It was suggested that the discrepancy between transport models and observations could be attributed to mobile colloids (naturally existing, small, <1 micron particles) in groundwater that act as carriers enhancing contaminant transport (McCarthy and Zachara, 1989) (Figure 1b). The low-solubility contaminants would adhere (sorb) to the mobile colloids and would migrate with groundwater. Neglecting to understand or account for this third phase in any conceptual transport model could significantly underestimate the mobility of strongly sorbing contaminants.

Colloids or nanoparticles are naturally occurring solids comprised of inorganic or organic material found in all groundwater and defined in size between 1 and 1000nm (Stumm, 1992). Colloids are often referred to as either pseudo-colloids or intrinsic (or eigen-) colloids. Pseudo-colloids are inorganic or organic colloids to which a radionuclide or contaminant has attached. Intrinsic colloids can form from specific actinides that hydrolyze to form an oxide or other pure phases. Ryan and Elimelech (1996) argued that three conditions must be met for colloidal (either pseudo or intrinsic) transport to occur: 1) colloids must exist, 2) contaminants must be associated with the colloids, and 3) both contaminants and colloids must move through the aquifer. It is now generally accepted that mobile inorganic or organic particles or colloids are ubiquitous in groundwater and that these solid materials have the potential to facilitate transport of contaminants (Kim, 1991; McCarthy and Degueldre, 1993). Increased understanding of the conditions under which colloids facilitate transport of radionuclides is necessary to help us to develop reliable transport models needed to predict radionuclide migration and improve models of risk assessment. The extent (how much, how fast, under what geochemical conditions) to which contaminants are transported via colloids as well as the mechanisms (e.g. adsorption, or surface precipitation onto mineral colloids,

coprecipitation or intrinsic colloid formation) control the rate of contaminant transfer through a given groundwater system. If colloids facilitate transport of low-solubility radionuclides, these contaminants will be detected at much higher concentrations down-gradient than simple solubility and retardation calculations would predict. Understanding colloid-facilitated transport of radionuclides is not only an issue for cleaning up legacy waste but also efforts to design safe, long-term, high-level waste repositories.



**Figure 1. A:** Contaminant transport in a two-phase system. Contaminants dissolved in water are mobile and contaminants sorbed to the host rock are 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. *Figure modified after Honeyman (1999).*

Radionuclides susceptible to colloid facilitated transport are strongly sorbing, low solubility elements. However, formation of an intrinsic or pseudo-colloid does not necessarily guarantee its transport. Other factors such as colloid filtration, stability, groundwater flow rate, groundwater chemistry, desorption/dissolution rates of the radionuclides are all important parameters that determine colloid facilitated transport of a specific radionuclide. The kinetics of sorption/desorption processes will largely determine pseudocolloid mobility (Saiers and Hornbeger, 1996). In order to assess the importance of colloids in the transport of radionuclides, the dominant processes under given geochemical conditions must be evaluated; colloid formation, and stability, radionuclide-colloid interaction and finally mobility. This

chapter focuses on our current progress in understanding the conditions and mechanisms that enhance colloidal transport and those that do not. Additional emphasis is given to field sites where investigations have shown colloids to facilitate the transport of radionuclides into the far-field.

## **10.2 Geochemistry and sorption behavior of radionuclides**

As mentioned in Chapter 1, the major sources of radionuclide contamination released to the environment come from nuclear weapons tests, production of nuclear fuels for weapons programs, nuclear power plants, and nuclear fuel processing plants. The major radionuclides of concern, based on half-life, toxicity, and abundance are the actinides (U, Np, Pu, and Am), and the fission products (Cs, Sr, Tc, and I). Many of these radionuclides can exist in multiple oxidation states and this has a profound effect on their solubility and sorptive capacity (Chapter 3). Radionuclides that might be soluble under certain groundwater conditions may be insoluble under other conditions.

Pu can exist in up to four oxidation states (+3, +4, +5, and +6), although under environmentally relevant conditions it is dominated by the most insoluble, Pu(IV) state (Chopin, 1983, Seaborg and Loveland, 1990). The presence of Pu(III) under reducing conditions has been identified by Kaplan (2007). However, Pu(III) is easily oxidized. The more soluble Pu(V) has been shown to reduce to Pu(IV) on the surface of organic and inorganic material (minerals or colloids) (Keeney-Kennicutt et al., 1985; Powell et al., 2005). Pu(VI) is favored in highly oxidic, high pH solutions. Under environmental conditions, Am occurs in the +3 oxidation state and is strongly sorbed to organic and inorganic material (Seaborg and Loveland, 1990). Cesium, is found in the +1 oxidation state and strongly sorbs to inorganic minerals. In addition to sorbing to soils and minerals, some radionuclides (e.g. Pu and Am) are highly reactive and can hydrolyze to form their own “intrinsic” colloids (Kim, 1986).

Other radionuclides such as Tc, I, U, Np, and Sr exist as dissolved ions in most groundwater and are mobile. Yet, variations in the redox conditions of the groundwater can change the behavior of these radionuclides. For example, <sup>99</sup>Tc most commonly exists in the

+4 and +7 oxidation states (Hu et al., 2008). Under oxidizing conditions, Tc(VII) will exist as the mobile pertechnetate ion ( $\text{TcO}_4^-$ ) in aqueous solution. Under reducing conditions it forms Tc(IV) species and its mobility can decrease due to sorption to minerals. Uranium occurs in the environment predominantly as U(VI) in oxic systems and U(IV) under reducing conditions. Uranium(IV) has low solubility, can form insoluble phases and is relatively immobile (Langmuir, 1997). The sorption of U(VI) is generally negligible at low pH and the strong affinity of uranyl ion for carbonate ions at higher pH effectively limits sorption (Kalmykov and Chopin, 2000). The behavior of  $^{129}\text{I}$  is also controlled by its chemical speciation. Iodine usually occurs as a highly mobile iodide ( $\text{I}^-$ ) ion, and has not been shown to significantly sorb to common minerals (Fuge and Johnson, 1986; Kaplan et al., 2000). Neptunium is also highly mobile in groundwater. At high pH values ( $>8$ ), Np complexes with carbonate ions in solution (Nakata et al., 2002). At pHs below 8, the pentavalent  $\text{NpO}_2^+$  species dominates. Under reducing conditions, Np(IV) has been shown to sorb to mineral surfaces or form a precipitate.

Based on the geochemistry of major radionuclides discussed above, Pu, Am, and Cs are the three most likely contaminants to sorb to colloids under oxidizing environmental conditions. Pu is of particular concern due to its large worldwide production inventory, high toxicity to human health and long half-life. It is estimated that there are more than 2200 metric tons of Pu worldwide stored as spent nuclear fuel, recycled Pu from nuclear power programs, nuclear weapons, past nuclear weapons testing and legacy waste (Hecker, 2011). Non-point sources include atmospheric weapons testing, and nuclear power plant accidents such as Chernobyl, Russia (1986) and Fukushima, Japan (2011). Point source distribution includes underground nuclear testing and legacy waste. The long half-life of Pu ( $^{239}\text{Pu} \sim 2.4 \times 10^4$  years) together with existing inventories guarantees that significant quantities will remain in our environment for a very long time. The world-wide source term for Am is significantly less than Pu. It is produced in nuclear detonations and from the decay of  $^{241}\text{Pu}$  ( $t_{1/2} = 14.4$  years). Its worldwide distribution is similar to Pu and it has both a point source and non-point source depositional history. Although less toxic shorter lived than Pu,  $^{137}\text{Cs}$  constitutes a major fraction of the current US radionuclide inventory from nuclear weapons processing, nuclear tests and reactor accidents. Cs exists in only one oxidation state and strongly sorbs to inorganic and organic material.

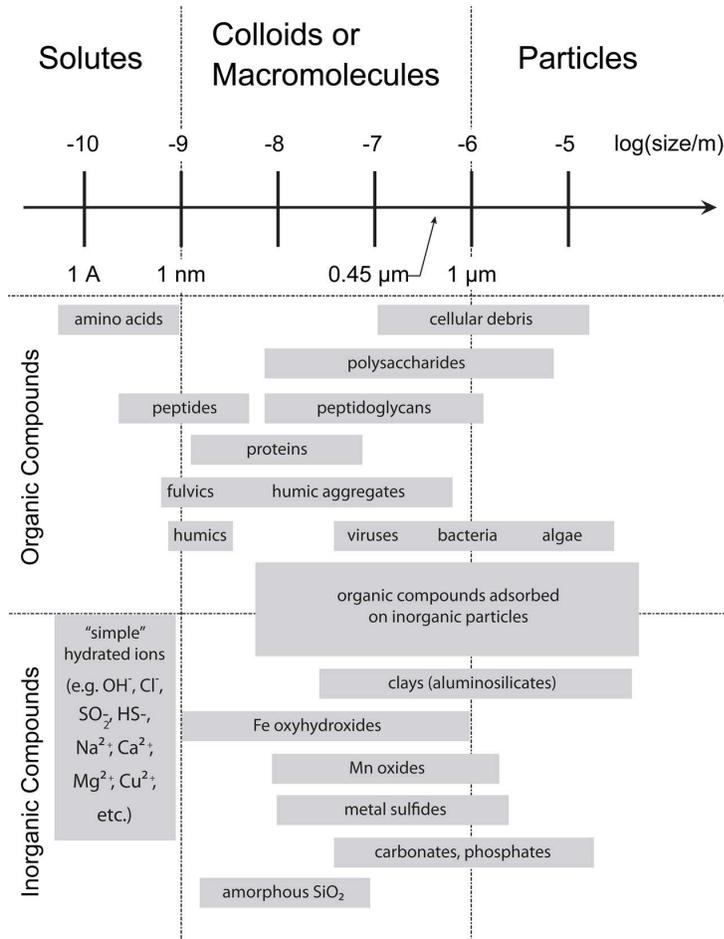
### 10.3 Nature and origin of colloids

As mentioned earlier colloids range in size between 1 and 1000 nm (Buffle and van Leeuwen, 1992; Stumm, 1992). Particles greater than 1000 nm are assumed to be relatively immobile because they do not remain suspended in water for a significant amount of time. Dissolved species are defined as less than 1 nm in size. As a result of their small size and low settling velocity, colloids can remain suspended via Brownian motion and transported with groundwater. Due to their large surface area per unit mass, colloids can also sorb significant quantities of contaminants (pseudocolloids). In practice, a 1 nm size cut-off separating dissolved from colloid materials is difficult to achieve in either laboratory or field measurements. As a result, when comparing data, it is important to know the specific procedures and definitions employed. For example, older studies used an arbitrary cut off of 0.45  $\mu\text{m}$  for colloidal vs. dissolved, even though many colloidal particles are  $< 0.45 \mu\text{m}$  in size. This cut-off is rarely used today. For a more in depth discussion of various colloid definitions, their advantages and limitations, see Wilkinson and Lead (2007a).

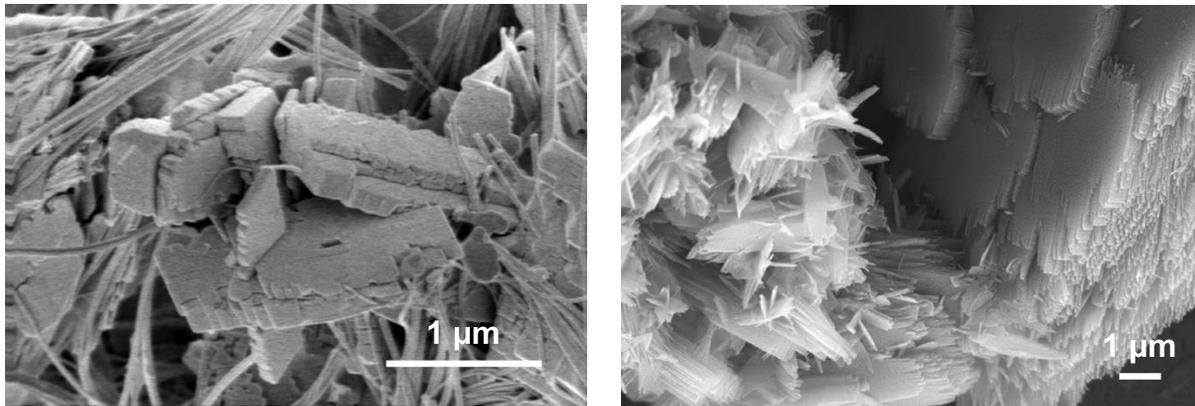
Natural colloids are found in all water and composed of inorganic minerals, organic species and microorganisms. Organic colloids are produced by microbial activity or the degradation of organic material in soil. Inorganic colloids are primarily generated by mechanical fragmentation of the host rock in contact with groundwater caused by either chemical or physical perturbations. Rapid infiltration of water through soils can induce shear that may generate colloids in both porous and fractured media. Colloid generation can also be induced by changes in groundwater flow rate. Degueldre et al. (1989) showed that colloids were continuously produced from water flowing through fractured granite at the Grimsel Test Site, Switzerland. Ryan and Gschwend (1994) investigated colloid release rates in the laboratory with a hematite-quartz system and showed that increased release rates were correlated with increases in flow rates.

Figure 2 shows a generalized size distribution of the different types of natural colloids that exist in nature. The true size distribution of different types of natural colloids are difficult to determine precisely because colloids do not necessarily occur as isolated entities and different types of colloids range in size (Wilkinson and Lead, 2007b). In addition, colloid

types can exhibit a size range of several orders of magnitude. Inorganic colloids consist of common minerals such as clays, zeolites, quartz, feldspars, Fe-oxides, and are usually reflective of the host rock, fracture lining minerals or mineral constituents of the soil (McCarthy and Degueudre, 1993). Figure 3 shows an example of clay and zeolite colloids produced from altered volcanic glass at the Nevada Test Site.



**Figure 2.** Size distribution of different types of environmental colloids, particles and dissolved species. *Modified after Wilkinson and Lead, 2007b*



**Figure 3.** Scanning electron images of colloids produced from incipient dissolution of nuclear melt glass from the Nevada Test Site. Inorganic colloids consist of clays and zeolites.

Organic colloids are composed of natural organic matter (NOM) resulting from the mechanical or microbial breakdown of plants and animals, microbial exudates, or turnover in microbial populations. Components of NOM can range from 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 acid, fulvic acids). As discussed in Chapter 5, NOM is extraordinarily complex. NOM has a wide range of chemical functionality, redox capacity, and molecular weight, so it is important to characterize its specific behavior in the presence of radionuclides. The size of humic acids alone can range from relatively simple low molecular weight organic acids in solution to large macromolecules or aggregates 100's of nm in size. Because NOM is not represented by a single organic species, its interaction with radionuclides will depend on the various compounds that constitute the NOM. Researchers have shown that sorption of Pu in systems containing NOM may be either increased or decreased, depending on the solution pH (Righetto et al., 1991). For example, the sorption of Pu(V) onto silica particles has been shown to be enhanced in the presence of microbially produced colloidal organic matter such as extracellular polymeric substances (Roberts et al., 2008). Sorption of metal ions to a mineral surface in the presence of humic acid is usually enhanced at low pH (formation of ternary humic acid-mineral-metal sorption complexes) and reduced at high pH (formation of humic acid-metal complexes). However, within the context of colloid-facilitated transport, the effect of NOM is complicated by the fact both ternary complexes that form at low pH and

binary complexes that form at high pH may or may not constitute a mobile colloidal phase, depending on the size range of the mineral and organic matter. Quantifying the reaction affinities and kinetics between radionuclides and the many organic compounds that constitute NOM is a formidable challenge. The reader is referred to Chapter 5 for a more in depth review of role of natural organics in the behavior of radionuclides.

Microorganisms are associated with a variety of radioactive materials at DOE sites and have been shown to affect the speciation and solubility of radionuclides (Barnhart et al., 1980; Francis et al., 1980; Fredrickson et al., 2004; Panak and Nitsche, 2001). Biochemical interactions between radionuclides and microorganisms are extraordinarily complex and can consist of a number of processes including external cell accumulation (sorption), internal cell accumulation, biomineralization, redox reactions, and ligand complexation (Neu et al., 2005). Understanding radionuclide-NOM interactions is only one of many reactions to be considered in systems containing microorganisms. As summarized in Chapter 6, microorganisms can affect the chemical speciation, solubility, and sorption properties of radionuclides resulting in either an increase or decrease in the concentrations available in groundwater. Bacteria also respond to environmental changes such as starvation and have been shown to have individual surface cell responses within a single population. As a result, bacteria require a fundamentally different description of radionuclide interactions with their surfaces than NOM or inorganic minerals.

As mentioned earlier, some transuranic elements such as Pu and Am can also hydrolyze to form intrinsic or eigen-colloids (Kim, 1991). These intrinsic colloids can form when the concentration of the actinide ions in solution exceeds the solubility product for the formation of a solid phase. If initial concentrations are high enough to form stable intrinsic colloids, then transport can occur independent of sorption or desorption to pseudocolloids. The solubility product of an actinide ion will depend on the oxidation state of the ion and the composition of the groundwater. Tetravalent actinide ions readily undergo colloid generation over a range of pH. The intrinsic Pu(IV) colloids ( $\text{PuO}_2$ ) form 2-5 nm nanoclusters (Soderholm et al., 2008) and remains stable in near-neutral solutions (Clark, 2000). Powell et al., (2011) showed that intrinsic Pu-oxide colloids form 2-5 nm crystalline colloids at pH 8. These colloids have the  $\text{PuO}_2$  fcc structure and once formed do not readily sorb to inorganic minerals, even in the presence of minerals with highly reactive surfaces, such as, goethite ( $\text{FeOOH}$ ). The second

strongest tendency to form colloids is the hexavalent actinyl ions, then trivalent, although this tendency is much less than An(IV) (Kim, 1991). Am(III) forms colloids in near neutral solutions but they are much less stable than Pu(IV) colloids and readily sorb to mineral surfaces (Kim, 1991). Between pH 3-7, Nagasaki et al., (1994) showed that Am forms stable colloids. Am complexes with carbonate ions in solution at pH>8. Pentavalent actinides undergo weak hydrolysis at high pH values and are generally soluble (Neck et al., 1992; Rao et al., 2004). Np(V) has not been shown to form colloids, remaining as a stable  $\text{NpO}_2^+$  ion in neutral solution. Batuk et al., (2011) investigated the sorption and speciation of U on silica colloids and determined that at surface coverage of <7%, no intrinsic colloids formed on the surface.

Although discussed separately above, the different colloid types (inorganic, organic, microbial, intrinsic) often exist together. The co-existence of several colloid types can change the behavior of a given radionuclide. In shallow groundwater where DOC concentrations are high, organic matter can coat inorganic minerals (Degueldre et al., 2000). In the presence of organic material, the sorption of Th(IV) to colloidal silica and iron oxide was enhanced (Artinger et al., 2000; Reiller et al., 2003). NOM can exist as both dissolved species or colloidal macromolecules. Microbes and organic compounds co-exist as microbes secrete organic compounds. Microbes have been shown to reduce Tc(VII) to Tc(IV) in the presence of Fe-bearing inorganic colloids (Peretyazhko et al., 2008). Teasing out the dominant biogeochemical processes in the presence of co-existing colloids and how the contaminant binds to the colloid is an active area of research. Chapter 8 discusses macroscopic sorption processes and the current state-of-the-art spectroscopic and geochemical modeling efforts being used to better understand the processes operating between radionuclides and the colloid solid/liquid interface.

#### **10.4 Colloid Characteristics**

Significant progress has been made in determining the abundance, composition, size and stability of colloids in natural waters in both porous and fracture media. These parameters help to determine the relevance of colloid-facilitated radionuclide migration. Measuring the concentration, size and composition of groundwater colloids from pumped wells is

challenging due to chemical and physical artifacts introduced from well construction and sampling (Puls et al., 1992). For example, well construction disturbs ambient groundwater conditions and can introduce new particles. Subsequently groundwater sampling can then yield artificially high colloidal loads. Well construction may also perturb the chemistry of the groundwater (pH, redox potential, etc), increasing or decreasing the stability of the original colloid population. In addition, high pump rates necessary to bring water samples to the surface have been shown to increase the concentration of colloids due to shearing from the aquifer walls (Puls et al., 1992). Where possible, gentle sampling, low purge and pumping rates were introduced into general protocols (Puls, 1995). In addition, after well construction more care is taken to make sure groundwater parameters are stabilized (e.g. pH, Eh, turbidity) prior to sampling.

When good sampling practices are employed and efforts to eliminate artifacts undertaken, the natural colloidal load measured in a variety of different geologic locations ranged from less than 1 mg/L to several hundred mg/L (Moulin and Ouzounian, 1992, Degueldre et al., 1996). In general, deeper groundwater has fewer colloids than in shallower systems. In deep groundwater collected from fractured granite at the Grimsel Test Site, colloid concentrations were low,  $\leq 1$  mg/L (Degueldre et al., 1989). Colloids separated from shallow groundwater in a sedimentary aquifer at the Hanford Site ranged in concentration from 14.75 to  $< 1$  mg/L (Dai et al., 2005). In another study where un-pumped flowing groundwater was collected from an abandoned mine, Filella et al. (2009) measured very low colloid concentrations between 0.12 to 0.029 mg/L. These low concentrations ( $< 1$  mg/L) may be more reflective of ambient conditions because the waters were not pumped. Higher measured concentrations may be more reflective of geochemically perturbed systems.

When looking at long-term, far-field transport, both saturated and partially saturated vadose zone environments need to be investigated. In the last 10 years, a considerable amount of research has focused on transport of colloids in partially-saturated vadose zone systems. Mobile colloids are ubiquitous in vadose zone environments with pore waters having concentrations up to 1000 mg/L during natural rainfall (DeNovio et al., 2004). Yet, how colloids move in partially saturated systems is even less well understood than for saturated environments. Wan and Wilson (1994) have shown that transport of colloids in partially-

saturated systems is a function of the interaction between the colloid and the air-water interface. Other processes for colloid transport in partially saturated porous media include transient infiltration events where colloids move episodically (de Jonge et al., 2004). For a review of colloid transport in porous media the reader is referred to DeNovio et al., (2004) and Wan and Wilson (1994).

Determining the size distribution of environmental colloids in efforts to estimate the surface area is also a difficult problem. Earlier efforts to determine the size distribution of colloids based on filtering techniques invariably lead to an over estimation of the larger colloid sizes as filters clogged preventing the smaller colloids from passing through the filters (Kersting et al., 1999). More recently, the size distribution of aquatic colloids has been investigated using techniques such as dynamic light scattering, flow-field flow fractionation (FFFF), or electron microscopy (Doucet et al., 2004 ). Analytical advances such as flow-field flow fractionation combined with on-line ICP mass spectrometry and size exclusion chromatography represent promising methods for determining the size distribution of groundwater colloids (Geckeis et al., 2003). Several studies have shown that groundwater colloids have a monomodal distribution of particles around 80 to 100 nm (Degueldre et al., 1996; Geckeis et al., 2003; Brachmann and Kersting, 2004), although all techniques show a long tailing down to a few nm. For further discussion, Wilkinson and Lead (2007a) provide an extensive comparison of the analytical techniques for measuring colloid concentration with the advantages and disadvantages of each method.

Stability of colloids in groundwater has a direct influence on concentration and mobility. The stability of colloids in a given aquifer is a function of pH, redox potential, water chemistry and hydrologic parameters. Degueldre et. al. (2000) studied the stability of inorganic colloids sampled from crystalline to sedimentary geologic formations, from fractured rock to vadose zone environments, from shallow to deep groundwater and from organic rich to organic poor systems. For steady state conditions, the chemistry of the water plays a major role in determining the stability of inorganic colloids. They found that alkaline element ( $\text{Na}^+$ ,  $\text{K}^+$ ) concentration below  $10^{-2}$  M and alkaline earth ( $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ) concentrations below  $10^{-4}$  M increase 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 decrease

inorganic colloid concentration by promoting coagulation (Roy and Dzombak, 1996). As discussed in Chapter 5, fulvic acids tend to be stable across all pH while humics are not stable at low pH.

### **10.5 Laboratory experiments of colloid facilitated radionuclide transport**

Laboratory transport experiments offer the advantage of studying relatively simple systems using a small number of controlled variables in an effort to provide a fundamental understanding of the system behavior without the natural complexity that exists in the field. Laboratory experiments, thus, can guide our conceptual understanding that can then be tested by field and modeling studies. Experiments discussed below were designed to evaluate if colloids pre-complex with low-solubility radionuclides would transport radionuclides on a laboratory scale under controlled hydro-geologic parameters.

Simulating transport through porous media using packed columns, Saiers and Hornberger (1999) conducted column experiments with quartz sand and kaolinite colloids that had been pre-sorbed with  $^{137}\text{Cs}$ . Under low ionic strength of the pore water, the kaolinite colloids accelerated the transport of  $^{137}\text{Cs}$  through the quartz columns. In a different study, the majority of Cs, pre-sorbed to colloids, was mobilized through Hanford sediments when the ionic strength of the groundwater was reduced (Fury et al., 2002). In a later study,  $^{137}\text{Cs}$  pre-equilibrated with colloids was eluted through a column with Hanford sediments under variable steady-state flow conditions (Chen et al., 2005). Depending on flow rate, greater than 70% of the  $^{137}\text{Cs}$  was stripped off the colloids and captured on the Hanford sediments, showing that the ability of colloids to enhance the transport of Cs is strongly dependent on the groundwater chemistry, desorption rates and the nature of the host material.

In another set of experiments, Artinger et al., (1998, 2002, 2003) showed that radionuclides that were pre-equilibrated with humic/fulvic acid colloids enhanced transport through sandy sediments compared to organic free sediment columns. Recovery rates were found to be a function of the solution residence time in the column suggesting that non-equilibrium, slow desorption rates determine long-term transport. Maes et al., (2006) and references therein conducted flow-through experiments to assess the ability of organic colloids to transport Am through a cored rock samples rich in clay and NOM. Americium was

initially complexed to organic colloids and then passed through Boon Clay cores contained in columns. The majority of the Am-NOM colloids dissociated and only a small fraction of the original Am migrated through the cores. In a second study, flow times were extended during the experiments and further desorption was observed. Although a small amount of Am that was initially complexed with colloids was mobile, the kinetics of slow desorption will ultimately determine mobility on a field scale.

In a series of fracture flow experiments, Zavarin et al. (2004) injected a radionuclide cocktail of dissolved radionuclide species through polished, zeolitized, rhyolitic tuff, 10 cm in length from the Nevada Test Site, NV. The radionuclides added to a low-ionic solution at pH 8 consisted of Pu(IV) ( $5 \times 10^{-9}$  M) Cs, Sr, U(VI), Np(V) and tritium. Less than 5% of the Pu was eluted through the columns. In a second set of fracture experiments, Pu(IV) was pre-equilibrated with zeolite colloids, then added to the radionuclide cocktail of dissolved Cs, Sr, U, Np and tritium. In this experiment approximately 30% of the Pu(IV) initially sorbed to the zeolite colloids was eluted through the tuff. Pu(IV) was transported more effectively when sorbed to inorganic colloids vs. dissolved.

The studies discussed above demonstrate that low-solubility radionuclides sorbed to colloids can migrate on a scale of 10's of centimeters in both porous media and a fracture flow systems. The studies also highlight the importance of the water chemistry and chemistry of the host medium through which these solutions travel in ultimately determining if the radionuclides are transported. If desorption rates are slow enough compared to groundwater flow rates, these radionuclides can migrate, but if the initial attachment of radionuclide to the colloid has a fast dissociation, transport of contaminants will not occur. Do these processes identified in laboratory experiments operate in more complex field environments where time scales and travel distances are longer?

## **10.6 Field studies of radionuclide migration**

Recent data on the transport of low-solubility radionuclides from four field sites are presented to illustrate the scale of colloid-facilitated radionuclide transport observed to date and the factors affecting those transport rates. The sites chosen are not exhaustive, but instead represent examples where low-solubility radionuclides have been deposited into the subsurface and have migrated. The four sites, the Nevada Test Site (Nevada), Rocky Flats

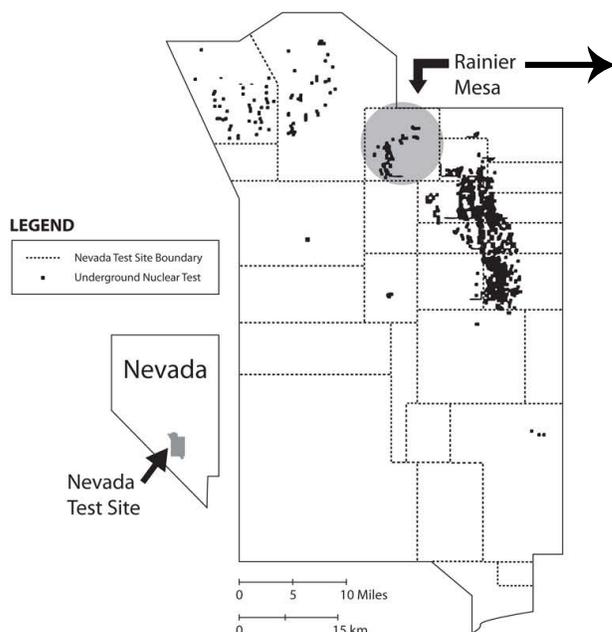
(Colorado), Mayak Production Facility (Russia), and Hanford Site (Washington), represent examples where contamination was released to the subsurface under a range of chemical conditions and into different biogeochemical depositional environments. The Nevada Test Site (NTS) was the U.S. proving ground for their nuclear testing program. Both Rocky Flats and the Hanford Site were production facilities for the U.S. weapons program. The Mayak Production Association was a reprocessing facility for the Russian nuclear weapon's program. Each site is characterized by a different geologic setting ranging from fractured volcanic rock, to sediments, from saturated fractured flow to vadose zone groundwater conditions.

### ***10.6.1 Nevada Test Site, NV U.S.A.***

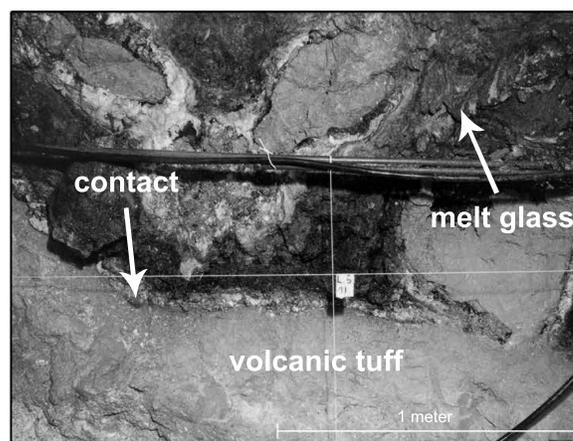
The Nevada Test Site (NTS) occupies 2,173 km<sup>2</sup> of desert and is located 105 km northwest of Las Vegas, USA. It was the location of over 800 underground nuclear tests conducted between 1956 and 1992 as part of the U.S. nuclear testing program and contains a large residual inventory of radioactive material deposited in the subsurface (Figure 4a) (Department of Energy, 2000). An estimated  $4.8 \times 10^{18}$  Bq ( $1.3 \times 10^8$  Ci) of radioactivity (calculated to 1992) remains in the subsurface, consisting of fission products (e.g., I, Tc, Cs, Sr), activation products (e.g., Eu, Co), actinides (e.g., Pu, Am, Np), and tritium (Bowen et al., 2001; Smith et al., 2003).

After a nuclear explosion, the surrounding rock is vaporized and the refractory material condenses at the bottom of the cavity in the form of nuclear melt glass (Figure 4b). Most of the refractory material (rare earths (Ce, Sm, Eu), alkaline earths (Mg, Sr, Ba) and actinides (Pu, Am) coalesce in the nuclear melt glass. In both the French nuclear tests in the South Pacific and the US tests at the NTS, > 95% of the residual Eu, Am and Pu was estimated to have been sequestered in the melt glass (IAEA, 1998, Rose et al., 2011). For the more volatile radionuclides (e.g. Tc, Cs, Co), a much smaller percentage is partitioned into the melt. For example, for both the French tests and the US tests at the NTS, approximately 60-70% of the <sup>137</sup>Cs was deposited in the rubble, above the melt glass. For more information on the phenomenology of a nuclear test see Kersting and Zavarin (2011) and references therein.

A



B



**Figure 4.** A. Map of the Nevada Test Site, showing the locations of over 800 underground nuclear tests. Circle denotes the location of tests in Rainier Mesa. B. Photo was taken after drilling back into the Rainier nuclear test cavity after detonation. The nuclear melt glass coalesces at the bottom of the cavity and contains greater than 95% of the actinides.

The geology of the NTS is complex with the majority of the nuclear tests detonated in alluvium or fractured rhyolitic volcanic rock. The groundwater is deep, roughly more than 250 m below ground surface and is predominantly Na-bicarbonate type, low ionic strength with a pH of  $\sim 8$ . Approximately 1/3 of the underground nuclear tests were detonated below the groundwater table, in fractured rhyolitic tuff.

In a pioneering study, Buddemeier and Hunt (1988) documented that the transition elements (Mn, Co) and lanthanide (Ce and Eu) radionuclides were associated with the colloidal fraction of the water collected 300m downgradient of the Cheshire nuclear test. In a later field study, Kersting et al. (1999) documented the unexpected appearance of low levels of Pu ( $2.3 \times 10^{-2}$  Bq) in addition to Cs, Co, and Eu, in the colloidal fraction of the groundwater, 1.3 km downgradient from the Benham nuclear test. Low levels of Am were also detected with the colloidal fraction (Thompson, 1999). Greater than 98 percent of the Pu

was associated with colloidal fraction of the groundwater. These two studies showed that inorganic colloids (clays and zeolites) can facilitate the transport of low solubility, strongly sorbing radionuclides significant distances in fractured volcanic rock where flow rates are fast (up to 80m/yr Blankennagel, 1973). Subsequent work analyzing the groundwater colloids from nine other wells at the NTS contaminated with radionuclides, reaffirms the observations that the overwhelming majority of the Pu detected in deep groundwater is low in concentration and associated with the inorganic colloidal fraction. In one study colloids separated from groundwater collected from the Chancellor nuclear test cavity contained 92% of the total Pu, and of that, ~70% was associated with smallest colloidal size fraction (10-100 nm) (Kersting and Zavarin, 2011).

In contrast to the majority of the groundwater samples collected in alluvium or fractured volcanic rocks at the NTS, water collected from the vadose zone (perched water system) in the tunnel system of Rainier Mesa contained radionuclides in the presence of high dissolved organic matter (DOM). Water samples had a DOM of 15-19 mg C/L compared to the local spring water of 0.2 mg C/L (Zhao et al., 2011). Tunnel construction (lagging, drilling fluids, wood debris, train diesel) and testing operations altered the water geochemistry resulting in elevated levels of DOM. Pu concentrations from these tunnels ranged from 2 Bq/L to  $3.3 \times 10^4$  Bq/L (54 pCi/L to  $9.0 \times 10^3$  pCi/L). In contrast to what has been observed in all the other groundwater wells at the NTS, less than 10% of the Pu detected in the groundwater was associated with the colloidal fraction (1000-20 nm). The majority of the Pu remained in the <20nm fraction. Experiments carried out to test the effect of DOM on Pu solubility showed that the Pu and Am  $K_d$ 's (distribution coefficient, see Chapter 3?) were up to 2 orders of magnitude lower in the vadose zone water with high DOM compared to the same waters with the DOM removed (Zhao et al., 2011). It is unclear whether this association is complexed in solution or sorbed to 1-20nm organic colloids. Np and U also detected in the tunnel waters was not strongly sorbed to the crushed rock and was also less affected by DOM, as only slightly lower  $K_d$ s were measured in the high DOM groundwater.

### 10.6.2 Rocky Flats, CO, U.S.A

The Rocky Flats Nuclear Weapons Plant (currently the Rocky Flats Environmental Technology Site) was established in 1951, approximately 24 km northwest of Denver, CO. The Rocky Flats plant manufactured pit components for use in nuclear weapons and purified Pu recovered from retired weapons (Clark et al., 2006). The plant was shut down in 1989 leaving behind a legacy of radiological waste including contaminated facilities, buried waste, buried waste pipelines, and Pu and U contaminated soil, surface water and shallow groundwater. One of the largest releases of Pu to the environment occurred when Pu-contaminated waste oil leaked from 3,750 drums stored outside from 1958 to 1968 (Kaiser-Hill, 2002). In 2007 the remediation of the site was completed and it was turned into a national wildlife refuge. Figure 5 shows a before and after picture of the Rocky Flats facility.



**Figure 5.** Two photos contrast the Rocky Flats Nuclear Weapons Plant (1952-1992) with its new designation in 2007 as the Rocky Flat National Wildlife Refuge. *From the Rocky Flats Cold War Museum.*

Rocky Flats is located in the semi-arid grasslands on the high plains of Colorado at the eastern edge of the Rocky Mountains. The groundwater table at Rocky Flats is deep, about 200-300 m below the surface, and isolated from the shallow groundwater. Shallow groundwater and surface water are inextricably linked as stream channels recharge the shallow groundwater and seeps discharge shallow groundwater to the surface (Kaiser-Hill, 2002).

In an initial study by Harnish and colleagues (1994), Pu was detected in shallow groundwater samples and associated with the colloidal fraction of the groundwater. More recently, Santschi and colleagues filtered surface waters and showed that the Pu and Am being transported was associated with Pu-organic ligand complexes as opposed to inorganic colloids (Santschi et al., 2002; Xu et al., 2008). Concentrations of Pu in surface waters ranged from  $7.8 \times 10^3$  to  $2.2 \times 10^3$  Bq/L (0.21 to 0.06 pCi/L). Virtually all the Pu is complexed by macromolecule ( $> 6\text{kDa}$ ,  $\sim > 1\text{nm}$ ) from degradation of siderophores.

### ***10.6.3 Mayak & Lake Karachai, Russia***

Located on the eastern slope of the Ural Mountains, the Mayak Production Association, Russia produced Pu for nuclear weapons by reprocessing spent nuclear fuel. Several inadvertent releases have resulted in significant contamination to the local area (Novikov et al., 2006). Several lakes and artificial reservoirs were used to discharge low and intermediate level radioactive waste that has subsequently leaked into soil and rock units and the nearby Techa River (Solodov et al., 1998). The rock units below Mayak are fractured andesitic to basaltic metavolcanic rocks, and in some areas, intensively fractured.

It is estimated that 4.44 GBq ( $1.2 \times 10^{-1}\text{Ci}$ ) of waste effluent containing  $^{90}\text{Sr}$ ,  $^{137}\text{Cs}$ ,  $^{239}\text{Pu}$  and  $^{241}\text{Am}$ , were discharged into Lake Karachai, originally an upland marsh with high organic content (Solodov et al., 1998). The effluents were weakly alkaline  $\text{NaNO}_3$  brine solutions with a pH between 7.9-9.3. Concentrations of Pu in the waste effluent at Lake Karachai were approximately 1000Bq/L ( $2.7 \times 10^4$  pCi/L) decreasing to 4.8Bq/L at 0.5 km distance and 0.029 Bq/L ( $7.8 \times 10^{-1}$  pCi/L) at 4.0 km down gradient (Novikov et al., 2006). Sr and Cs have migrated from Mayak, but no colloid studies have been undertaken. Novikov et al., (2006) showed that Pu detected 4 km from the source was associated with Fe-oxyhydroxide colloids. At a distance of 2km approximately 75% of the Pu was associated with the colloidal fraction; increasing to  $> 90$  at 3.2 km. Of the colloidal fraction, 70-90% of the Pu was associated with the smallest size 3-10 kD size filter ( $\sim 1-15$  nm). Although the Pu was clearly associated with inorganic colloids at the distal wells ( $>90\%$ ), the aqueous Pu was higher at near-field wells (25%) suggesting that the complex depositional chemistry of the releases may have played an initial role in Pu migration. The Am was not associated with the colloidal fraction (personal

comm. Kalmykov). In contrast, all the U and 70-80% of the Np was in the dissolved fraction (< 3kD).

#### ***10.6.4 Hanford, WA, U.S.A.***

The Hanford Site was established in 1943 as part of the U.S. weapons program to produce Pu for nuclear weapons. Located in the semi-arid, 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 basalts (Zachara et al., 2007). Groundwater movement in the highly permeable sediments is generally toward the Columbia River with the water table estimated between 230 and 270 m bgs.

Hanford Site processed about 95,000 metric tons of uranium fuel and produced 67 metric tons of Pu for use in nuclear weapons (National Academy Sciences, 2001). Separating the Pu produced in reactors generated large volumes of radioactive waste. Subsurface release of radionuclides and hazardous chemicals came from: 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 pH, salinity, radionuclide composition and concentration. Of the tanks, approximately 50 percent of the single-walled tanks have leaked (Zachara et al., 2007). It is estimated that approximately  $2.4 \times 10^8$  to  $0.8 \times 10^8$  GBq ( $6.5 \times 10^6$  to  $0.22 \times 10^6$  Ci) of high-level waste was discharged to the soil from releases and leaking tanks, and of this, approximately  $4.4 \times 10^5$  GBq ( $1.2 \times 10^4$  Ci) was  $^{239}\text{Pu}$  (Felmy et al., 2010). Other strongly sorbing radionuclides include Sr, Cs, Am, Co (National Academy Sciences, 2001).

At the Hanford Site, Dai et al. (2004) used low flow pumping techniques to examine the concentration and distribution of colloids in several shallow groundwater wells near known Pu releases in the 100 Area, where groundwater has a pH between 7 and 8. They detected very low levels of Pu (from below detection to  $10^{-4}$  pCi/Kg) in several of the groundwater wells demonstrating that the Pu inventory that was previously released into the vadose zone has yet to reach the groundwater in appreciable quantities. Seven to twenty-nine percent of the Pu measured in the groundwater was associated with the colloidal fraction (1 kDa-

200nm). The organic content of the groundwater samples was not reported. Other ongoing studies of actinides detected at high concentration in vadose zone sediments.

#### **10.6.5 Evidence for colloid facilitated migration of low-solubility radionuclides**

These field studies demonstrate that despite differences in water chemistry, initial depositional history and geo-hydrologic setting, inorganic and organic colloids can and do play an important role in facilitating the transport of low-solubility radionuclides. It is important to note that in these field studies, where the radiologic source terms are large, the concentrations of radionuclides detected in groundwater are routinely very low suggesting and that the actual mass fraction of radionuclides transported is small.

### **10.7 Summary and future research needs**

In the last 10-15 years, tremendous advances have been made in our understanding of the extent to which colloids facilitate the transport of radionuclides, yet we are still not at a level of understanding that permits us to predict the behavior of radionuclides under various geo-hydrologic environments. In summary:

- Colloids are ubiquitous in groundwater with their concentrations a strong function of groundwater chemistry and hydrology. Colloid concentrations are minimized in high ionic strength groundwater.
- Field studies under oxic conditions, where ionic strength is low, and flow rates are high, both inorganic and organic colloids have transported low solubility radionuclides (Cs, Pu and Am). Under these same field studies Np and U are not colloidally transported.
- In general, the concentrations of low-solubility radionuclides measured in field studies are extremely low, suggesting that the mass fraction of radionuclide that has been transported is quite low.
- Bench scale colloid transport experiments have shown that the fraction of radionuclide transported through the columns can decrease with increasing contact time, suggesting

that the desorption rate are critical in assessing the significance of migration on the field scale.

- The co-existence of several colloid types has been shown to alter the overall mobility of a given radionuclide compared to the presence of just one colloid type. For example, the presence of organics with inorganic colloids has been know to both increase and decrease the stability of radionuclides, depending on the groundwater conditions.

In order to understand the dominant conditions under which colloids facilitate transport of radionuclides more controlled field-scale studies are needed where the source term is known, and the fraction of contaminant transported can be calculated under varying colloidal and hydro-geologic conditions. This is especially important for the design of high-level-waste repositories. Currently the nature of radionuclide interactions at the colloid/water interface is not well understood, yet critical to understanding the kinetically controlled desorption processes and that ultimately determine long-term mobility. In environments where the initial concentration of contaminants is high, a more complete understanding of the stability of intrinsic colloids is needed. It is important to keep in mind that we have learned much from recent research in the area of colloid-facilitated transport and that tomorrow's laboratory, field or modeling studies will undoubtedly help us to develop further a more complete understanding so that reliable transport models can be developed.

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