

**COLLOID-FACILITATED TRANSPORT OF  
RADIONUCLIDES IN NATURAL GROUNDWATER  
SYSTEMS—LITERATURE REVIEW**

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## ABSTRACT

Assessments of the postclosure performance of the potential high-level waste repository at Yucca Mountain, Nevada suggest that colloid-facilitated transport of highly sorbing radionuclides may be an important contributor to the peak dose at long time frames (greater than 100,000 years). There are, however, a number of conservative assumptions included in current abstractions of colloid-facilitated transport. These assumptions are associated with uncertainties in the factors and parameters representing colloid sorption, filtration, and the potential for irreversible sorption of radionuclides onto colloids. To help identify and understand these and other important colloid-facilitated transport uncertainties and to help identify experimental approaches and designs to investigate these uncertainties, recent (after 1990) technical literature was gathered and reviewed. This report lists collected recent technical literature pertinent to the study of colloid and colloid-facilitated transport in natural groundwater systems and briefly summarizes recent findings from the literature. Brief discussions are included on the topics of colloid stability, colloid retention, sorption of radionuclides onto colloids, and colloid deposition and mobilization. Based on a review of the collected literature, several topics are identified as potential areas of detailed work to address uncertainties in the current Yucca Mountain performance assessment abstractions of colloid transport. These topics areas include (i) evaluation of the nature of early breakthrough of colloids; (ii) investigation of the extent of sorption of radionuclides onto colloids in solutions of complex chemistry or in solutions containing species that may compete for sorption sites; and (iii) evaluation of the effects of chemical transients on colloid release, among others.

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# 1 INTRODUCTION

Radionuclides that sorb strongly to minerals in the subsurface also tend to have strong affinity for the naturally occurring mineral colloids that are present in small concentrations within groundwater. In the absence of colloids, strongly sorbing radionuclides are relatively immobile. Once attached to colloids, however, the radionuclides have reduced interactions with the porous medium and may move relatively unretarded through the subsurface.

Colloid-facilitated transport of radionuclides is of interest and concern for the long-term geological disposal of high-level waste at the potential Yucca Mountain repository. In its colloid technical basis document, the U.S. Department of Energy (DOE) suggests that colloids found in natural groundwater systems must remain stable for tens of thousands of years and avoid filtration and sorption into the surrounding rock matrix in order to play a significant role in contaminant transport (Bechtel SAIC Company, LLC, 2003). Yet there are numerous indications that natural groundwater colloid populations are stable (e.g., Allen, et al., 2003), and strongly sorbing nuclides such as plutonium have been observed to be associated with colloids in groundwater and are suspected to have been transported over kilometers via colloid-facilitated transport (e.g., Kersting, et al., 1999; Allen, et al., 2003). Despite the potential importance of colloids to the transport of highly sorbing radionuclides, such as plutonium, numerous uncertainties exist in many aspects specific to colloid transport.

The Risk Insights Baseline Report (NRC, 2004) concludes that colloid-facilitated transport in the natural system is of medium significance to waste isolation based on the potential for colloids to enhance transport of the strongly sorbing actinides americium and plutonium. Performance effects of colloid-facilitated transport have not yet been assessed with the Total-system Performance Assessment (TPA) Version 5.1 code, which is currently under development, but an earlier version of the TPA code was used to bound the effects by assigning no retardation to americium, plutonium, and thorium. That conservative analysis indicated colloid-facilitated transport could increase dose at 10,000 years by nearly two orders of magnitude in comparison to the basecase. In addition, sorption in the alluvium—a process potentially affected by the presence of colloids—was concluded to be of high significance to waste isolation. The U.S. Nuclear Regulatory Commission (NRC) (2004) also recognizes that colloid transport in the geosphere is subject to significant uncertainties and recommends that additional analyses be undertaken to identify more realistic approaches for colloid-facilitated transport. DOE analyses have also identified colloid-facilitated transport as a potentially important contributor to dose, and colloid-facilitated transport is included in the current DOE Total System Performance Assessment (Bechtel SAIC Company, LLC, 2003). Recent analyses of colloidal transport in the saturated zone suggest colloid-associated breakthrough of plutonium will occur after about 100,000 years (Bechtel SAIC, LLC, 2004).

Recent analyses by Painter and Cvetkovic (2004) and Painter, et al. (2002) have assessed the potential effects of colloid-facilitated transport on the barrier capabilities of the saturated zone. Among the conclusions of Painter and Cvetkovic (2004) were (i) colloid-facilitated transport is likely the dominant saturated zone transport mechanism for highly sorbing radionuclides, (ii) the rate of permanent immobilization of colloids and the desorption rate of radionuclides from colloids were the most sensitive parameters in transport simulations, and (iii) because of uncertainties in colloid transport, bounding, or conservative assumptions may be used by implementers of performance assessments.

## 2 OBJECTIVES AND SCOPE

A literature review was conducted to (i) ensure the Center for Nuclear Waste Regulatory Analyses (CNWRA) staff had access to recent and relevant scientific literature covering the transport of colloids through natural systems, (ii) examine potential experimental methods and designs to investigate and quantify important colloid transport parameters, and (iii) identify appropriate experimental equipment useful for colloid transport experiments.

The detailed literature survey and review focused on colloid-facilitated radionuclide transport in natural systems. The review objectives were to assemble information available in the published scientific literature and, to the extent possible, include data available through federal, state, and other government or private databases. Pertinent literature sources, guided by the key areas of review noted below, were compiled and evaluated. The evaluation was designed to include a report summarizing the relevant content of important literature sources along with an outline describing recommended approaches (both methods and equipment) for evaluating colloid-facilitated radionuclide transport in natural systems using laboratory or intermediate-scale experiments.

The key areas of review to guide literature search content are

- Colloid production and stability in natural groundwater systems
- Colloid filtration in natural groundwater systems—saturated and unsaturated
- Sorption and desorption processes—including sorption of radionuclides onto colloids, sorption of colloids onto geologic materials, and rates of sorption and desorption
- Colloid transport mechanisms
- Laboratory and field-scale (physical) experiments designed to evaluate colloidal transport mechanisms
- Colloidal transport mechanisms in areas having subsurface geological conditions similar to those found at Yucca Mountain, Nevada (i.e., oxidizing, low organic carbon content, low ionic strength)
- Published colloid-facilitated radionuclide transport research applicable to Yucca Mountain, Nevada

The key Information to be considered in the Evaluation and Recommendations Report includes

- Results and findings of past studies
- Laboratory and field methods and approaches for studying/quantifying colloidal transport and equipment necessary to conduct field or laboratory studies
- Procedures for quantifying colloidal transport other than optical (e.g., isotope tracers)—information on quantifying nonradioactive particles is particularly important
- Colloidal transport in areas having subsurface geological conditions similar to Yucca Mountain



### 3 METHODS

Several sources of information were reviewed as part of this literature survey. Initially, several colloid-related research articles, previously collected as part of other CNWRA activities, were examined. The articles and the references contained therein were reviewed and used as a guide for subsequent research activities. This preliminary review was followed by an examination of two websites: (i) the Licensing Support Network ([www.lsnnet.gov](http://www.lsnnet.gov)), a database of documents related to the planned DOE application for a license to construct a high-level waste repository at Yucca Mountain, Nevada; and (ii) that of the Office of Civilian Radioactive Waste Management ([www.ocrwm.doe.gov](http://www.ocrwm.doe.gov)) and its links to technical documents related to Yucca Mountain.

The final source of information reviewed was the published body of literature (e.g., articles and laboratory reports) collected through the use of search engines, journal archives, and various research databases. In conjunction with this phase of the survey, references included in pertinent articles were also examined as a source of further information. Additional research efforts were focused on locating international publications, conference proceedings, and other research materials not readily available for review.

In the following sections, results of the literature review are organized according to primary research topic. Additionally, the full collection of references used to prepare this report is included at the conclusion of the document.

## 4 COLLOID PRODUCTION

Colloids, defined as ranging between one nanometer and one micrometer in size, are capable of sorbing considerable quantities of contaminants due to large specific surface areas {on the order of  $10^4$  to  $10^5$  m<sup>2</sup>/kg [ $4.9 \times 10^4$  to  $5 \times 10^5$  ft<sup>2</sup>/lbm]} and high specific surface energies (Filella and Buffle, 1993; Lieser, et al., 1990; Lu, et al., 2000). Colloids may form stable complexes with various pollutants, including radionuclides, that, without colloidal transport would otherwise have limited mobility in the subsurface (Crist, et al., 2005). Colloid production is the initial step in colloid-facilitated transport of radionuclides. Three types of colloids are commonly described in the literature—groundwater colloids, real colloids, and pseudocolloids—each with differing methods of colloid production. Several excellent reviews provide discussions of colloid generation mechanisms (e.g., McCarthy and Zachara, 1989; Kim, 1994; Zhao and Steward, 1997; Kretzschmar, et al., 1999). A brief discussion of these colloid types and their production is included here.

### 4.1 Groundwater Colloids

Groundwater colloids are naturally occurring, can be composed of organic and inorganic materials, and remain in suspension due to relatively large surface area to molecular mass ratios (Kim, 1991; Lieser, et al., 1990; Filella and Buffle, 1993). The existence of groundwater colloids increases the surface area available for radionuclide sorption, and mobilization of these colloids allows for transport of sorbed radionuclides (Bechtel SAIC Company, LLC, 2003).

Production of groundwater colloids can be described in three steps: genesis, stabilization, and transport (McGraw and Kaplan, 1997; McCarthy and Zachara, 1989). Four different mechanisms of colloid genesis are identified in McGraw and Kaplan (1997): (i) translocation from overlying soils, (ii) dissolution of iron oxides or calcium carbonates which release otherwise stationary particles and may produce subsequent precipitation downgradient of dissolution, (iii) dispersion of particles due to chemical changes in groundwater, and (iv) precipitation (McGraw and Kaplan, 1997). Chemical precipitation is often a result of weathering of mineral phases followed by an accumulation of elements and changes in chemistry that induce supersaturation of groundwater with respect to an easily precipitated mineral phase (McCarthy and Zachara, 1989).

The organic constituents that form colloids are produced from the soil or from organic deposits within the sediments (McCarthy and Zachara, 1989). Inorganic colloidal constituents are commonly produced as the result of mechanical abrasion or chemical precipitation (Allen, et al., 2003). Mechanical abrasion can result from a chemical or physical disturbance, such as a change in redox conditions, rapid water infiltration, or a change in the groundwater flow rate. Groundwater colloids are often then mobilized by changes in the groundwater chemistry or by groundwater flow transients (Allen, et al., 2003; Kretzschmar, et al., 1999). Experimental findings suggest stabilization is a function of the three-way interaction of ionic strength, pH, and sodium adsorption ratio (SAR) (McGraw and Kaplan, 1997; Kretzschmar et al., 1999). Finally, the stabilized colloids may be transported in the groundwater if attachment mechanisms (i.e., straining, blocking, gravitational settling, sorption) are minimized or do not occur (McGraw and Kaplan, 1997).

## **4.2 Real Colloids**

Real colloids (also known as true or intrinsic colloids) are defined as an aggregation of hydrolyzed ions and are particularly significant for actinides. In natural groundwater systems, most actinide ions are easily hydrolyzed (Kim, 1994). Specifically, actinides in the +4 oxidation state have high charge-to-radius ratios and readily hydrolyze to form complex ions with increased stability (Runde, 2002). The primary step of hydrolysis is followed by polymerization, and ultimately, the generation of real colloids (Zhao and Steward, 1997). Formation of real colloids is determined by the initial actinide concentration and will likely occur in the presence of significant amounts of tetravalent actinides (Runde, 2002). Real colloids are not considered in the most recent DOE Total System Performance Assessment for Yucca Mountain because these colloids are expected to dissolve under the expected solution chemistry conditions (outside of the waste package) of the potential repository (Bechtel SAIC Company, LLC, 2003).

## **4.3 Pseudocolloids**

Pseudocolloids consist of organic or inorganic groundwater colloids with sorbed ions (Kim, 1991). Actinide ions have the tendency to sorb strongly to groundwater colloids due to the hydrolysis properties of actinide ions at neutral pH (Kim, 1994). Hydrolyzed actinide ions may combine with the groundwater colloids through ion exchange, surface complexation, or a substitution reaction. After sorption, the chemical properties of pseudocolloids remain similar to the properties of the groundwater colloid (Zhao and Steward, 1997). Sorption of radionuclides to groundwater colloids can enhance radionuclide transport by potentially reducing the effects of matrix diffusion or sorption to matrix surfaces (van de Weerd and Leijnse, 1997; Baek and Pitt, 1996).

Naturally occurring groundwater colloids of clays, silica, and zeolites have been found in Yucca Mountain groundwater, and experiments have been conducted to evaluate the nature of reversibility/irreversibility of radionuclide sorption on these colloids and iron oxyhydroxide colloids (Lu, et al., 2000). Pseudocolloids with actinides reversibly or irreversibly sorbed are the main type of colloid considered in the most recent DOE Total System Performance Assessment for Yucca Mountain (Bechtel SAIC Company, LLC, 2003).

## 5 COLLOID STABILITY

In assessing whether colloid-facilitated transport is a significant means for the transport and release of radionuclides from the potential repository, DOE concludes that colloids must remain stable over long distances and extended periods of time to contribute significantly to dose and be important to the system performance (Bechtel SAIC Company, LLC, 2003). However, model analyses of colloid-facilitated transport suggest that when reversible sorption processes are considered, colloids can contribute to the mobility of radionuclides even if individual particles are not transported over long distances (Cvetkovic, et al., 2004; Painter and Cvetkovic, 2004). Moreover, there is significant evidence to support that groundwater colloids in natural systems are indeed stable (McCarthy and Zachara, 1989; Kretzschmar, et al., 1999).

In current performance assessment models, DOE assumes that pseudocolloids (naturally occurring groundwater colloids with attached radionuclides) will be stable at the typical ionic strength and pH values of Yucca Mountain saturated zone waters (Bechtel SAIC Company, LLC, 2003). The stability of iron oxide colloids in the DOE performance assessment model is dependent on ionic strength and highly dependent on pH, with these colloids predicted to be unstable in the pH range from 8 to 9 (Bechtel SAIC Company, LLC, 2003). Although there is direct experimental evidence for iron oxide colloid instability in this pH range, some studies have shown that the stability and transport of iron oxide colloids can be significantly enhanced, even near the pH of the zero-point of charge (~8.5), when anionic species are sorbed to the iron oxide surface (Puls and Powell, 1992). Whether or not this is an issue for Yucca Mountain waters should be evaluated, especially in light of the potential for technetium to be released from the waste form as an anionic species.

### 5.1 Factors Affecting Colloid Stability

There are multiple factors affecting the stability of colloid suspensions and numerous experimental findings documenting these factors. Factors affecting stability can be divided among chemical conditions, physical conditions, and intercolloidal electrical forces. These factors are described in the following sections.

#### 5.1.1 Chemical Conditions

Colloid stability is in part a function of chemical conditions of the groundwater (i.e., pH, salinity, ionic strength) and the chemical and physical character of the colloid (e.g., colloid surface charge and colloid size). The ionic strength of groundwater is particularly important to colloid stability. High ionic strengths are associated with low colloid concentrations and the settling of colloidal suspensions (Bechtel SAIC Company, LLC, 2003). Experiments have shown that colloid stability has increased when solution concentrations of alkali metals and alkaline earth metals are below  $10^{-2}$  and  $10^{-4}$  M, respectively (Degueldre, et al., 2000). Additionally, at high salt concentrations ( $>0.1$  M NaCl), a fast aggregation rate has been observed, while a slower rate was observed at moderate salt concentrations (0.01–0.1 M NaCl) (Abdel-Fattah and El-Genk, 1998).

To compensate for excess surface charge, cations in an electrolyte solution will associate with the surfaces of negatively charged colloids, while anions will associate with surfaces of positively charged colloids (Zhao and Steward, 1997). As ionic strength increases and ions in

the solution are more prevalent, the net colloid surface charge is reduced significantly (Zhao and Steward, 1997; Lieser, et al., 1990). Once the local surface charge and repulsive electrical forces are reduced, the colloid particles can aggregate (Lieser, et al., 1990).

If the ionic strength of the solution remains constant, colloidal stability will depend primarily on the pH of the solution (Mori, et al., 2003). The pH-sensitive range for stability of colloids is dependent on the colloid composition and is a result of surface charge effects. The surface charge of a colloid generates repulsive forces preventing aggregation and settling; thus, the greater the surface charge, the more stable the system (Zhao and Steward, 1997). Surface charges are dependent on pH, ionic strength, and the presence of dissolved organic matter (Zhao and Steward, 1997; Song, et al., 1994). The pH of zero-point of charge is defined as that pH where colloids have zero surface charge. As the solution pH deviates from the pH of zero-point of charge, the surface charge increases and the suspension stabilizes (Zhao and Steward, 1997). Typically, colloids are more stable in solutions with pH values significantly different than the pH of zero charge of the colloid. For instance, iron oxyhydroxide colloids, which have a composition-dependent pH of zero charge that ranges from about six to nine, are most stable in solutions with pH values below six or above nine. Similarly, the stability of smectite colloids increases as solution pH increases away from a pH of zero charge of about two. Groundwater colloids also may adsorb hydrogen and hydroxide ions dependent on the acidity or causticity of the solution, which produces corresponding positive, neutral, or negative surface charges. Modeling of the first few hundred years postclosure of the potential Yucca Mountain repository suggests only 6 percent of near-field waters will have a pH and ionic strength that will produce stable colloid suspensions. For the remaining stable solutions, the high temperatures will lead to water evaporation and an increase in ionic strength, causing settling of the colloid particles (Bechtel SAIC Company, LLC, 2003; Triay, et al., 1995). This will result in lower colloid concentrations and fewer colloids available for the transport of radionuclides.

The presence of organic materials has a stabilizing effect on inorganic colloids (Allen, et al., 2003). In some cases, sorption of radionuclides onto the solid matrix can be enhanced by the interaction of humic acid with the solid phase (Righetto, et al., 1991). Deviations in the behavior of plutonium in the absence of humic acid are likely due to transformations in oxidation state of the plutonium from the typical tetravalent state (Righetto, et al., 1991). Organic substances are present at Yucca Mountain, but the measured concentrations of total organic carbon are low, ranging from about 0.15 to 0.5 mg/L [ $2 \times 10^{-5}$  to  $6.7 \times 10^{-5}$  oz/gal] in water from Well J-13 (Allen, et al., 2003; Bechtel SAIC Company, LLC, 2003; Triay, et al., 1996). Furthermore, the presence of calcium in the groundwater at Yucca Mountain should reduce the complexation capacity of humic acid, thus reducing the potential influence of humic acid on radionuclides (Runde, 2002; Runde, et al., 2002).

### **5.1.2 Physical Conditions**

Colloid physical characteristics, such as their size, also affect their stability. Although the potential of particles to settle from suspension due to gravity is directly related to the particle size, stability increases with size because of a reduction in the number of colloid collisions for a given mass concentration of colloids (i.e., the smaller the colloid, the larger the particle count and the higher the probability of collision between colloids) (Haber and Brenner, 1993; Bechtel SAIC Company, LLC, 2003). The size of a colloid is often determined by the formation rate of the nuclei and the growth rate of aggregates (Zhao and Steward, 1997). If the formation rate is

slow and the aggregation rate fast, the result will be a small number of large particles. Conversely, if the formation rate is fast and the aggregation rate is slow, the result will be a large number of small particles (Zhao and Steward, 1997). For larger particle sizes  $\{>1000 \text{ nm } [3.9 \times 10^{-2} \text{ mil}]\}$ , gravitational settling will generally overcome both electrostatic repulsion and the effects of fewer, less frequent collisions (Allen, et al., 2003).

### **5.1.3 Intercolloidal Electrical Forces**

Stabilization of colloids is also dependent on repulsive electrical forces between colloids. These forces are a function of colloid concentration, density, size, composition, and surface chemistry. The forces are also determined by van der Waals attractive forces, which are based on the distance of separation between colloids and the size of the colloid particles. The shorter the distance between the colloids and the smaller the size of the colloids, the greater the van der Waals forces (Bechtel SAIC Company, LLC, 2003).

With increasing temperature and ionic strength, the strength of the repulsive forces between colloids decreases, and van der Waals attractive forces become increasingly influential, causing instability (Bechtel SAIC Company, LLC, 2003). The increase in temperature alone, measured by an increase in the kinetic energy of the particles, causes instability due to increased colloid-colloid collisions, which leads to aggregation (Bechtel SAIC Company, LLC, 2005).

One theory predicting colloidal stability based on electric forces is the Derjaguin, Landau, Verwey and Overbeek theory, which predicts stability for different geometric configurations based on electric repulsive forces and van der Waals attractive forces (McCarthy and Zachara, 1989). The total interaction energy, as a function of separation distance, is the sum of these forces (Kretzschmar, et al., 1999; Elimelech and O'Melia, 1990). The Derjaguin, Landau, Verwey and Overbeek theory accurately predicts stability for colloids of low surface charge (e.g., silica) or for very smooth, uniform, hydrophobic, and hydrophilic surfaces (Snoswell, et al., 2003). When the electric repulsive forces dominate, the particles are stabilized and dispersed in suspension (McCarthy and Zachara, 1989). Conversely, aggregation of colloids or colloid-solid attachment occur when van der Waals forces are the dominant force. Experimental results do not appear to match predictions based on the Derjaguin, Landau, Verwey and Overbeek theory when the electric repulsive forces are dominant (Mills, et al., 1991).

## **5.2 Experimental Findings on Colloid Stability**

Numerous laboratory-scale experiments have investigated factors controlling colloid stability. In general, experiments indicate that decreases in ionic strength lead to the production of colloids and stabilization of existing colloids (Kretzschmar, et al., 1999). Experiments also demonstrate the stability, and ultimately the concentration, of colloids in solution decrease due to aggregation and flocculation with increases in solution ionic strength (Allen, et al., 2003).

For example, Mori, et al. (2003) conducted stability experiments with Febex bentonite colloids at ionic strengths from 0.001 M to 0.22 M utilizing sodium chloride, sodium perchlorate, or calcium chloride solutions. The hydrodynamic mean diameter of the bentonite colloids was determined as a function of ionic strength using dynamic light scattering. With increasing ionic strength and a nearly constant pH (final pH of approximately  $8.7 \pm 0.5$ ), as ionic strength increased from 0.01 M to 0.22 M, an increase in the size of bentonite colloids was noted, indicating aggregation. Similarly, in experiments conducted at constant ionic strength

( $5 \times 10^{-3}$  M), Mori, et al. (2003) noted colloid aggregation increased as pH was lowered to values below 6.5. They concluded that stability of smectite colloids may be quite sensitive to pH changes due to development of differing charges on edge sites (positive) versus planar sites (negative) as pH is lowered.

In a second example, Triay, et al. (1996) utilized kaolinite clay and amorphous silica colloids to determine the effects of ionic strength on colloid stability. After preparation of the silica and kaolinite clay, the hydrodynamic mean diameter and concentration were noted for silica {85 nm [ $3.3 \times 10^{-3}$  mil] and  $1.75 \times 10^9$  particles per mL} and kaolinite clay {140 nm [ $5.5 \times 10^{-3}$  mil] and  $1.59 \times 10^9$  particles per mL}. The particles were suspended in solutions of 0.368-mM sodium carbonate and 10.6-mM sodium bicarbonate with a pH of 7.8. Sodium chloride was added to induce aggregation and produce a final NaCl concentration of 100–800 mM. Autocorrelation photon spectroscopy measurements were utilized to determine the initial particle aggregation rate constant. Specific equipment used to obtain measurements included a Brookhaven laser light scattering system (Brookhaven Instruments Corporation, Holtsville, New York) containing an Innova 90 Argon laser (Coherent Laser Products Division, Palo Alto, California) at a wavelength of 514 nm [5140 Å] and 0.5 to 1.0 W. The measurements were obtained with a scattering angle of 90 degrees. Sampling times were determined based on particle concentration and ionic strength with the hydrodynamic diameter measured every minute with a sampling duration of 30 seconds. The experimental findings identified differences in the stability behavior of the two types of colloids. Clay colloids became unstable at lower electrolyte concentrations than silica colloids. Additionally, clay colloids displayed a gradual transition from stability to instability, rather than the immediate transition displayed by the silica colloids. Triay, et al. (1996) also noted an increase in the rate of aggregation with increases in ionic strength.

## 6 COLLOID FILTRATION

The nature of and degree to which colloids experience filtration will affect their ability to facilitate radionuclide transport. In a summary of colloid transport processes included in their current performance assessment model for Yucca Mountain, DOE states that one condition that must be met for colloid-facilitated transport to be considered a significant transport mechanism is “radioactive colloids must not be appreciably filtered, reversibly or irreversibly, by the host rock (Bechtel SAIC Company, LLC, 2003).” However, depending on the rate of reversible sorption of radionuclides on colloids, irreversible sorption (filtration) of colloids onto the host rock may not prevent effective colloid-facilitated transport of radionuclides (Painter and Cvetkovic, 2004). Where reasonable technical bases are available, DOE includes colloid removal via colloid sorption or filtration (Bechtel SAIC Company, LLC, 2003). This includes filtration at rock layer interfaces (based on colloid and pore size distributions) of colloids with irreversibly attached radionuclides traveling in the unsaturated porous matrix. DOE also includes reversible sorption of colloids onto the surfaces of rock matrix pores or alluvium (Bechtel SAIC Company, LLC, 2003). Approximately 95 percent of pore spaces in the tuffs at Yucca Mountain have pore throat sizes between 0.01 and 0.1  $\mu\text{m}$  [ $3.9 \times 10^{-4}$  and  $3.9 \times 10^{-3}$  mil], with the larger pores in the unsaturated zone predicted to be dry and unsuitable for colloid transport (Baek and Pitt, 1996). Thus, the tuff matrix can potentially reduce the concentration of colloids through filtration, especially within the unsaturated zone beneath Yucca Mountain (Bechtel SAIC Company, LLC, 2003).

In general, two types of filtration can occur during colloidal transport through rock matrix or small fractures: physical straining and film straining. Several experimental studies have been conducted to determine the factors affecting filtration.

### 6.1 Physical Straining of Colloids

There are two types of physical straining mechanisms that occur during the transport process in a porous matrix: (i) filtration or straining due to size and (ii) filtration due to physical-chemical forces.

#### 6.1.1 Size Exclusion

Physical straining is the dominant mechanism of colloid retention in porous media and depends upon the dimensions and geometries of pores relative to the size of the colloid (Bradford, et al., 2005; McCarthy and Zachara, 1989). As colloids move through the rock matrix, pores of varying sizes are encountered. If these pores are smaller in size than the colloid, the colloid will not be transported through the pore, resulting in the plugging of the pore (Bechtel SAIC Company, LLC, 2003; Sen, et al., 2002). Plugging of the pore causes a reduction in flow velocity and possible retardation of colloidal transport (Sen, et al., 2002). Furthermore, if smaller colloids enter the pore, the colloids will likely come in close proximity to each other, enhancing the chances for aggregation and formation of larger particles that may get trapped within the pore (McCarthy and Zachara, 1989).



### **6.1.2 Physical-Chemical Forces**

Since groundwater colloids are generally small in size, other processes of filtration may be more influential in the reduction of colloid concentration (McCarthy and Zachara, 1989). One of these processes is physical-chemical filtration, which consists of two steps: collision and attachment. Collision of colloid particles is dependent on sieving, diffusion, and sedimentation (Wan and Tokunaga, 1997). Sedimentation effects may be important, especially for silica colloids (Bechtel SAIC Company, LLC, 2004). Attachment of colloid particles to the rock matrix is controlled by electrostatic, chemical, or van der Waals forces. Attraction can be avoided by minimal surface collisions due to slow transport rates or movement through preferential pathways at relatively high velocity. Since rock matrices are generally negatively charged and colloids are favorably attracted to oppositely charged matrices, positively charged colloids will primarily be attracted and filtered by the rock matrix, whereas negatively charged colloids tend to remain in solution (McCarthy and Zachara, 1989).

### **6.2 Film Straining of Colloids**

Both conventional physical straining and film straining are dependent on particle size. As saturation levels decrease, the connectivity of water between pores and the thickness of water films are reduced. When colloids are larger than the thickness of water film coating the rock, film straining occurs (e.g., McGraw and Kaplan, 1997; Keller and Sirivithayapakorn, 2004). Colloids may also become immobilized by deposition at the air–water–rock interface (Wan and Tokunaga, 1997; Bechtel SAIC Company, LLC, 2003). As the ratio of the water film thickness to colloid diameter decreases filtration of colloids increases.

### **6.3 Experimental Results**

A significant number of experimental and modeling studies have evaluated factors and effects of colloid filtration on colloid transport. Several recent studies are included in this literature review (e.g., Higgs, et al., 1993; Kretzschmar and Sticher, 1998; Kretzschmar, et al., 1999; Puls and Powell, 1992; Grolimund, et al., 1998; Song and Elimelech, 1993; Gao, et al., 2004). The two papers reviewed below provide examples of the discrepancies in predictions of modeling approaches that rely on the assumptions and concepts of the Derjaguin, Landau, Verwey and Overbeek theory (see Section 5.1.3) and experimental observations of colloid transport in unsaturated conditions (McGraw and Kaplan, 1997; Wan and Tokunaga, 1997).

McGraw and Kaplan (1997) conducted experiments under saturated and unsaturated conditions to determine the effect of colloid size and degree of saturation on filtration. Glass chromatography columns {5 cm [2 in] inner diameter by 10 cm [4 in] length} were used in experiments conducted under saturated conditions, and an Unsaturated Flow Apparatus (a modified ultracentrifuge) was utilized for experiments conducted under unsaturated conditions. Prior to the experiments, model simulations of colloid transport under saturated conditions indicated colloidal particles with diameters between 200 and 500 nm [ $8 \times 10^{-3}$  and  $2 \times 10^{-2}$  mil] had the highest probability of being transported through a sandy matrix without being filtered. However, results of the filtration experiments conducted under saturated conditions using polystyrene colloids with diameters ranging from 52 to 1,900 nm [ $2 \times 10^{-3}$  to  $7.5 \times 10^{-2}$  mil] did not indicate any significant size-dependent differences in the initial breakthrough and time to reach  $C/C_0$  of 0.5. Retention and recovery of the colloids was more related to the hydrophobic

or hydrophilic nature of the colloids used. Similar experiments conducted under unsaturated conditions did exhibit a difference in breakthrough and retention based on colloid size. There was an exponential decrease in the percent mass of colloids recovered as colloid size increased. Retention of the colloids in unsaturated conditions was interpreted to be primarily a result of film straining, although the hydrophobicity of colloids had a minor influence on the results. Hydrophilic colloids appeared to be preferentially transported. McGraw and Kaplan (1997) concluded that for unsaturated conditions with low volumetric water content (approximately 6 percent for the conditions at Hanford) only the smallest colloids {<60 nm [ $2.4 \times 10^{-3}$  mil]} would be transported. Once these small colloids reached the saturated zone they would be especially susceptible to the effects of diffusion because of their size. It is interesting to note that the majority of natural system colloids collected from the Nevada Test Site and near Yucca Mountain appear to be of sizes ranging from 60 to 200 nm [ $2.4 \times 10^{-3}$  to  $8 \times 10^{-3}$  mil] (Allen, et al., 2003; Triay, et al., 1996; Bechtel SAIC Company, LLC, 2003).

Wan and Tokunaga (1997) conducted a similar set of filtration experiments at variable saturations in sand-packed columns. Their results also showed a direct dependence on colloid size and efficiency of filtration (via film straining) at lower water saturations. Colloids with diameters less than the predicted film thickness moved freely through columns at all saturation levels. An important aspect of this study (and that of McGraw and Kaplan, 1997) is that predictions of hydrophilic colloid deposition based on Brownian motion and conventional filtration theory, which would predict enhanced deposition of the smaller colloid sizes, are opposite the observed outcome (Wan and Tokunaga, 1997).

## 7 SORPTION OF RADIONUCLIDES TO MOBILE SURFACES

Sorption of radionuclides to colloids can be described as an assortment of physical or chemical interactions between the radionuclide and the colloid (Bechtel SAIC Company, LLC, 2003; Dozol and Hagemann, 1993). Factors affecting the sorption and sorption rates of radionuclides to colloids and a summary of experimental results are discussed in the following paragraphs.

### 7.1 Factors Defining Sorption

Sorption of radionuclides to colloidal surfaces is dependent on several factors such as electrostatic forces, ion exchange, surface reactions, and co-precipitation (Bechtel SAIC Company, LLC, 2003). For instance, the rate and magnitude of sorption of plutonium to colloids is dependent on the oxidation state of plutonium, while uranium sorption onto colloids is significantly affected by the pH, alkalinity, and ionic strength of the solution (Triay, et al., 1997). The quantity of radionuclides capable of sorbing to colloids is determined in part by the available surface area of colloids and the concentration of colloids within a system. The large specific surface area of colloids can enable significant sorption of radionuclides, even in the presence of low concentrations of colloids (Lu, et al., 1998). DOE has concluded that analyses of groundwater at Yucca Mountain indicate colloid concentrations are too low for significant transport of sorbed radionuclides (Bechtel SAIC Company, LLC, 2003). Thus, unless sorption of radionuclides to colloids is irreversible or slowly reversible relative to colloid travel times, and a significant fraction of colloids is transported through the system, colloid-facilitated transport of radionuclides may not be significant (Allen, et al., 2003; Painter, et al., 2002). Sorption of plutonium and americium to colloids has been shown to be irreversible or slowly reversible (Penrose, et al., 1990; Lu, et al., 1998, 1997; Wittman, et al., 2005).

Sorption of radionuclides onto colloids may be modeled as reversible or irreversible, and the effective reversibility of sorption is determined by the rate of sorption, desorption, and transport (Wittman, et al., 2005). As colloids with sorbed radionuclides are transported through an aquifer, the radionuclides may desorb from the colloids to establish equilibrium between the colloids and the rock matrix (Bechtel SAIC Company, LLC, 2003; Mills, et al., 1991). Sorption of radionuclides is often modeled as a linear, reversible process, but this modeling approach relies on three assumptions. First, the water–radionuclide–colloid system must be in thermodynamic equilibrium. Second, the rate of sorption must be linear with respect to the concentration of radionuclides. And third, the presence of other solutes in the system must not affect the sorption. Studies of radionuclide sorption onto colloids (e.g., Penrose, et al., 1990; Lu, et al., 1998, 1997; Wittman, et al., 2005; Runde, et al., 2002) indicate that actinide sorption onto colloids may not be linear or reversible. Moreover, definitive rates for plutonium and americium sorption to colloids and desorption from colloids are not well constrained (Bechtel SAIC Company, LLC, 2003). The importance of the relative rates of radionuclide sorption and desorption is also dependent on the regulatory compliance period of the potential repository (Painter and Cvetkovic, 2004). Additional experimentation, similar to the experiments discussed in the following sections, should be conducted to examine the reversibility of sorption.

## **7.2 Experimental Results Regarding the Sorption Behavior and Rates of Radionuclide Sorption Onto Colloids**

Numerous sorption experiments have been conducted and documented with specific information regarding sorption rates. Although Dozol and Hagemann (1993) argue that predicting the exact sorption behavior of an ion under certain conditions is impossible, in general, sorption onto colloids occurs rapidly while desorption occurs at much slower rates (Dozol and Hagemann, 1993; Bechtel SAIC Company, LLC, 2003). For instance, plutonium, americium, uranium, and cesium sorb more strongly to bentonite colloids than bulk bentonite. This is likely due to the large specific surface area of the colloids. Sorption of other radionuclides, such as selenium, technetium, and neptunium to colloids is much less significant (Mori, et al., 2003).

Varying approaches and methods were utilized to determine the quantity of radionuclides sorbed to and desorbed from colloids. Radionuclide concentrations were measured by inductively coupled plasma mass spectroscopy and alpha- and gamma-spectrometry or sodium iodide gamma spectroscopy (Mori, et al., 2003; Lu and Mason, 2001). Other techniques measured the radionuclide concentrations based solely on the alpha activity of the solution using a liquid scintillation counter or kinetic phosphorescence analyzer (Lu, et al., 2000, 1997). Further experiments utilized flow field flow fractionation followed by inductively coupled plasma mass spectroscopy to determine the size, composition, and interaction of colloids with trace elements (Baalousha, et al., 2006).

Lu, et al. (2000, 1998, 1997) determined the amount of radionuclides sorbed to colloids by centrifuging a sample after the contact period expired, then filtering the supernatant fluid and analyzing it for radioactivity. Corrections were made based on activity readings measured before and after centrifuging and filtering. The difference between the initial and final activity measurements determined the quantity of radionuclides sorbed. Similar procedures were conducted to determine the rate of desorption. The samples were obtained from the sorption experiments, and the colloids were extracted after varying time periods. The activity of the extracts was measured, and the rate of desorption was calculated based on the difference between the initial and final activities (Lu, et al., 2000, 1998, 1997).

### **7.2.1 Experiments Focusing on the Sorption Behavior of Plutonium**

The majority of experiments conducted have focused on the sorption behavior of plutonium with the experimental methods generally utilizing the same technology discussed in Section 7.2. Batch experiments conducted included the use of Oak Ridge centrifuge tubes or other closed polyethylene containers, usually with an orbital shaker set at 150–300 revolutions per minute during the contact period between colloid and radionuclide. Upon completion of the contact period, the supernatant was extracted, sometimes filtered, and analyzed for activity (Allen, et al., 2003; Lu, et al., 2000, 1998, 1997; Runde, et al., 2002).

Generally, experimental findings note the rate of sorption of plutonium (V) is slow, while the sorption rate of plutonium (IV) is rapid. The rate and extent of plutonium sorption to hematite, goethite, smectite, and silica colloids varies due to differences in surface characteristics (Allen, et al., 2003; Lu, et al., 1998).

Some experiments compared the rates of adsorption of differing oxidation states (i.e., IV and V) of plutonium onto hematite and goethite colloids. Lu, et al. (1997) measured sorption of plutonium (V) and plutonium (IV) onto mineral colloids in natural groundwater. The plutonium (IV) used in these experiments was known to be in the form of true colloids. The overall percentage of sorption of plutonium (V) sorbed onto iron oxide colloids was greater than that measured for plutonium (IV), but the overall  $K_d$  values were of the same magnitude (Lu, et al., 1997; Allen, et al., 2003). The adsorption rate of plutonium (IV) was found to be rapid and independent of time, while the adsorption rate of plutonium (V) was found to be time dependent. Subsequent experiments also indicated the sorption rate of plutonium (IV) (not in true colloid form) to clinoptilolite was high, but the magnitude was dependent on pH, with the lowest magnitude of sorption occurring between a pH of 7 and 9.5 (Allen, et al., 2003). Others studied the sorption behavior of plutonium (V) and noted that its sorption as measured by  $K_d$  (in mL/g), varied over a range of five orders of magnitude, with a minimum  $K_d$  of about 20 mL/g [35 in<sup>3</sup>/oz] for calcite and a maximum of about  $6 \times 10^6$  mL/g [ $1 \times 10^7$  in<sup>3</sup>/oz] for goethite (Allen, et al., 2003). Minerals commonly found as natural groundwater colloids in the Yucca Mountain region—montmorillonite, clinoptilolite, and silica—had typical plutonium (V) sorption values of about  $10^3$  mL/g [1,700 in<sup>3</sup>/oz] (Allen, et al., 2003). Similar to plutonium (IV), plutonium (V) sorption varied with pH, with sorption minima near pH of 8 (Allen, et al., 2003).

Lu, et al. (1998) conducted extensive experiments with colloidal plutonium (IV) (in true colloid form) and soluble plutonium (V) in the presence of hematite, goethite, smectite, and silica colloids in J-13 water. These experiments also examined effects of organic matter and surface area. Results of the experiments indicated the sorption rate of plutonium (V) to hematite, goethite, or smectite colloids in natural groundwater could be modeled as a first order reaction with the rate dependent on the plutonium concentration. The rate of sorption was slower in natural groundwater than in synthetic groundwater. The difference was interpreted to be due to the presence of dissolved organic carbon in natural groundwater. During the sorption process, organic matter, silicon, and calcium were sorbed by hematite, goethite, and smectite colloids, respectively (Lu, et al., 1998). Thus, the presence of silicon and calcium may affect the sorption of plutonium. The surface area of colloids also affected the rate of sorption for plutonium (V). Goethite used in this study had a larger surface area, and thus, a higher sorption rate than hematite. The slower sorption rate of plutonium onto smectite colloids was interpreted to result from the difference in external versus internal surface area of the smectite colloids. Eighty percent of the measured surface area of the smectite colloids is internal, thus smectite has a smaller external surface area and a slower sorption rate (Lu, et al., 1998). The sorption mechanism for plutonium (IV) to the four types of colloids likely involves electric binding and particle interactions. Electric binding is the electrostatic sorption of negatively charged colloids to charged plutonium (IV). Since hematite, goethite, and smectite colloids have a higher negative charge than silica colloids, a stronger attraction exists between these colloids and plutonium (IV) (Lu, et al., 1998).

Lu, et al. (2000) conducted additional sorption experiments using plutonium, americium, neptunium, and uranium in the presence of hematite, montmorillonite, and silica colloids in J-13 groundwater. These experiments studied the effects of temperature, ionic strength, and colloid concentration on adsorption. In general, the results of experiments conducted with differing actinides showed that americium exhibited the highest sorption coefficients, irrespective of the type of colloid studied. Neptunium and uranium exhibited the lowest sorption coefficients. Table 7-1 summarizes the adsorption distribution coefficients obtained from Lu, et al. (2000).

<b>Table 7-1. Maximum Adsorption Distribution Coefficients (mL/g*) in Natural Groundwater</b>			
	Hematite	Montmorillonite	Silica
Americium	$1.0 \times 10^7$	$1.0 \times 10^5$	$2.1 \times 10^4$
Neptunium	$8.8 \times 10^2$	$2.2 \times 10^2$	$5.5 \times 10^2$
Plutonium	$1.1 \times 10^5$	$5.8 \times 10^3$	$8.1 \times 10^3$
Uranium	$4.4 \times 10^2$	$1.9 \times 10^2$	$5.8 \times 10^2$
*mL/g = 1.73 in <sup>3</sup> /oz			

The effects of temperature on the adsorption rate and magnitude of sorption were examined by Lu, et al. (2000) and Runde, et al. (2002). Lu, et al. (2000) noted that the quantity of actinides sorbed to colloids in natural groundwater increased with increases in temperature. Similar temperature-oriented experiments (Runde, et al., 2002) noted that an increase in temperature from 20 to 80 °C [68 to 176 °F] increased the sorption of neptunium on hematite, montmorillonite, and silica colloids by 20 percent and increased the adsorption distribution coefficient one order of magnitude {from approximately  $10^2$  to  $10^3$  mL/g [170 to 1,700 in<sup>3</sup>/oz]}. In contrast, sorption of plutonium did not increase as significantly with changes in temperature—except for montmorillonite colloids, where plutonium sorption increased by 38 percent (Runde, et al., 2002).

Sorption experiments have also been conducted at varying ionic strengths (Lu, et al., 2000). In general, increasing ionic strength had only slight effects on the adsorption rates of plutonium and americium to hematite colloids, with greater effects on sorption of plutonium and americium to montmorillonite and silica colloids. Increasing ionic strength only slightly influenced adsorption of neptunium to hematite and montmorillonite colloids, but significantly influenced the adsorption of neptunium to silica colloids.

Results of experiments in which colloid concentrations were varied in natural groundwater indicated the adsorption distribution coefficient of plutonium and americium to hematite, montmorillonite, and silica colloids was significantly higher at low colloid concentrations than at high colloid concentrations (Lu, et al., 2000). The decreased adsorption of radionuclides at high colloid concentrations was interpreted to be caused by aggregation, which occurs at high colloid concentrations and results in less surface area (Lu, et al., 2000).

Plutonium (V) sorption experiments produced rapid sorption kinetics followed by a gradual increase over time with final adsorption distribution coefficients of  $9.3 \times 10^4$  mL/g [ $1.6 \times 10^5$  in<sup>3</sup>/oz] for hematite,  $5.8 \times 10^3$  mL/g [ $1.0 \times 10^4$  in<sup>3</sup>/oz] for montmorillonite, and  $8.1 \times 10^3$  mL/g [ $1.4 \times 10^4$  in<sup>3</sup>/oz] for silica (Runde, et al., 2002). Identical experiments conducted with neptunium produced lower final distribution coefficients of 880 mL/g [1,520 in<sup>3</sup>/oz] to hematite, 150 mL/g [260 in<sup>3</sup>/oz] to montmorillonite, and 550 mL/g [950 in<sup>3</sup>/oz] to silica colloids after 240 hours (Runde, et al., 2002). Since plutonium (V) and neptunium (V) are chemically similar, the investigators concluded the stronger sorption behavior exhibited by

plutonium (V) indicated a more complex interaction mechanism than that of neptunium (V) (Runde, et al., 2002). In addition, the sorption distribution coefficient of plutonium increased 2 to 4 times when colloid concentration in groundwater was decreased from 200 to 10 mL/g [340 to 17 in<sup>3</sup>/oz]. This effect was interpreted to be caused by colloid aggregation that reduced the available surface area (Runde, et al., 2002).

Batch experiments conducted to determine the rate of desorption have employed the same technology as used in sorption experiments. In general, colloids with sorbed radionuclides are continuously shaken with an orbital shaker for a specified contact period. The solutions are centrifuged, supernatant is extracted, and the activity of radionuclide(s) in the supernatant measured (Allen, et al., 2003; Runde, et al., 2002; Lu and Mason, 2001; Lu, et al., 1998, 1997).

Numerous experiments have indicated that the majority of plutonium sorbed to colloids remains attached despite changes in the pH, and thus can effectively be transported with colloids (Allen, et al., 2003). For example, Lu, et al. (1997) demonstrated that desorption of plutonium (IV) and (V) from iron oxide colloids was slow and small in magnitude, with less than 0.01 percent of either oxidation state desorbing from the colloids after 30 days. Desorption of plutonium (IV) from clinoptilolite colloids was also noted to be slow, with 2–8 percent desorbing over 7 months (Lu, et al., 1997). In a separate experiment, plutonium remained strongly sorbed on hematite colloids, with less than 1 percent desorbing after 290 days (Runde, et al., 2002). On the other hand, 21 percent of plutonium desorbed from montmorillonite and silica colloids during the same time frame (Runde, et al., 2002). Experimentally determined maximum distribution coefficients following desorption in J-13 groundwater were estimated at  $1.2 \times 10^7$  mL/g [ $2.1 \times 10^7$  in<sup>3</sup>/oz] for hematite colloids,  $1.1 \times 10^4$  mL/g [ $1.9 \times 10^4$  in<sup>3</sup>/oz] for goethite colloids,  $3.8 \times 10^3$  mL/g [ $6.6 \times 10^3$  in<sup>3</sup>/oz] for smectite colloids, and  $1.3 \times 10^3$  mL/g [ $2.2 \times 10^3$  in<sup>3</sup>/oz] for silica colloids (Lu, et al., 1998).

Fracture transport experiments have indicated differences in the nature and rates of desorption of radionuclides from colloids when measured in batch experiments versus transport experiments (Kurosawa, et al., 2004; Allen, et al., 2003). Experiments described in Allen, et al. (2003) showed plutonium desorbed more rapidly from montmorillonite and silica colloids during transport through a fracture than predicted by batch experiments. The authors suggest that fracture surface minerals (e.g., manganese oxides) may effectively compete with colloids for plutonium; this does not seem to occur in batch experiments (Allen, et al., 2003). It is hypothesized that desorption rates increased in fractures due to collisions between the colloids and fracture walls. The collisions allow for the direct transfer of the colloids to the surface matrix, rather than a multistep transfer process involving desorption from the colloid, transport to the surface matrix, and sorption to the matrix (Allen, et al., 2003).

### **7.2.2 Experiments Focusing on the Sorption Behavior of Other Radionuclides**

Mori, et al. (2003) conducted batch experiments with radionuclides and various colloids (such as Grimsel granodiorite, fracture in-fill materials, and Febex Bentonite colloids). Experimental findings indicated nearly constant distribution coefficients of  $7 \times 10^3$  mL/g [ $1.2 \times 10^4$  in<sup>3</sup>/oz] for americium and cesium after short contact periods. Experiments using other radionuclides showed significant increases in sorption over longer contact periods with a distribution coefficient of about  $1 \times 10^6$  mL/g [ $1.73 \times 10^6$  in<sup>3</sup>/oz] after 3 weeks for plutonium and  $1.5 \times 10^3$  mL/g [ $2.6 \times 10^3$  in<sup>3</sup>/oz] after 12 weeks for uranium.

Batch sorption experiments were conducted by Missana, et al. (2004) on cesium in alkaline, granitic groundwater of low ionic strength from the Grimsel Test Site. The experiments were performed in an anoxic glove box under nitrogen atmospheric conditions with supernatant activity measured using a sodium iodide gamma detector (COBRA, Canberra). Experimental findings indicated significant nonlinear sorption of cesium and uranium onto bentonite colloids. Also, desorption of the cesium and uranium was identified as not completely reversible (Missana, et al., 2004).

Kurosawa, et al. (2004) performed batch and column transport sorption experiments on cesium to sodium bentonite colloids for varying contact periods (1, 3, 5, and 7 hours and 1, 3, 5, and 7 days). Measurements of the quantity of cesium sorbed were performed using ultrafilters (with molecular weight cutoffs of 10,000 Daltons). Experiment results were important because cesium desorption from the bentonite colloids was greater during transport through a column than was observed in batch experiments.

Sorption experiments were conducted by Lu and Mason (2001) using smectite, hematite, and montmorillonite colloids and Sr-85, which was used as an analog for Sr-90, the third most abundant radionuclide in groundwater at DOE facilities. The experimental setup utilized Oak Ridge centrifuge tubes and an orbital shaker at 150 revolutions per minute with varying contact periods (1, 4, 24, 48, 96, and 240 hours). After the contact period, the samples were centrifuged and supernatant collected for measurement of strontium activity using sodium iodide gamma spectroscopy. Sorption of strontium onto the colloids was strong and rapid, with the majority occurring within the first hour of contact. Desorption was slow, with the strontium sorbed onto the silica colloids completely desorbed with 90 days.

Experiments conducted by Lu and Mason (2001) indicated that the presence of calcium ions in J-13 groundwater, possibly competing with strontium, caused the release of increased quantities of sorbed strontium from montmorillonite and silica colloids. Lu and Mason (2001) concluded that calcium, sodium, and other cations in solution may compete with strontium for sorption sites despite the large surface area of the silica colloids utilized in the experiment.



## 8 SORPTION OF COLLOIDS TO IMMOBILE SURFACES

Two separate methods of sorption to immobile surfaces have been defined: favorable and unfavorable deposition (Ryan and Elimelech, 1996). Favorable deposition involves the settling of colloids onto rock surfaces in the absence of repulsive forces or when dominant attractive forces are present (Ryan and Elimelech, 1996). The rate of deposition to the rock surface is governed by the rate of transport to the surface. In contrast, unfavorable deposition occurs in the presence of repulsive forces, with the rate of deposition controlled by colloid interactions (Ryan and Elimelech, 1996). In general, sorption of radionuclides and colloids onto the rock matrix may alter the surface properties and the association and dissociation constants of the matrix (van de Weerd and Leijnse, 1997). In natural groundwater systems, the pH range is such that both the colloid and rock matrix are typically negatively charged. Thus, the attraction and subsequent attachment, should it occur between the colloid particle and the rock matrix, is often weak (Degueudre, et al., 1996; Chen and Flury, 2005). Sorption of colloids to surfaces may also be dependent on colloid size in natural groundwater systems (Bechtel SAIC Company, LLC, 2003). Sorption of colloids onto immobile surfaces differs somewhat in the saturated and unsaturated zones due to the presence of the air–water interface within the unsaturated zone. The sorption behaviors of colloids to immobile surfaces in both zones are discussed in the following paragraphs, followed by a summary of relevant sorption experiments.

### 8.1 Sorption of Colloids in the Saturated Zone

Sorption of colloids to the solid–water interface under saturated conditions has been interpreted to occur through a complex two-step process, with an initial transport step followed by an attachment step (Abdel-Fattah and El-Genk, 1998). During the initial transport step, the colloid moves close to the immobile surface by Brownian diffusion, sieving, or gravitational sedimentation (Bechtel SAIC Company, LLC, 2003). The kinetics of transport are dependent on colloid size, density, accessible surface area, pore structure and flow velocity (Kretzschmar, et al., 1999). Others note that transport is also dependent on diffusion (Elimelech and O’Melia, 1990).

The second step, attachment, is determined by short-range interactions between surfaces of the colloid and matrix (e.g., Chen and Flury, 2005). Near-surface interactions are determined by the magnitude of forces, which are dependent on water chemistry, colloid and matrix composition, surface chemistry, and water flow rate (Bechtel SAIC Company, LLC, 2003). The kinetics of attachment are controlled by the magnitude of interactions between colloids and the rock surface, with these interactions defined by chemical characteristics of the colloid–matrix interface and solution chemistry (Elimelech and O’Melia, 1990). For the kinetics to be independent of the chemistry and solely dependent on the collision rate, the solution must be at a critical deposition concentration (usually related to a particular solute, such as NaCl) and above a certain ionic strength such that the repulsive energy barrier is diminished, and every collision favors attachment (Kretzschmar, et al., 1999).

### 8.2 Sorption of Colloids in the Unsaturated Zone

The transport behavior of colloids can be affected by the presence of continuous and discontinuous air–water–solid interfaces in the unsaturated zone. Sorption of colloids to the air–water–solid interface also includes a two-step process of transport and transfer or

attachment, similar to that discussed in Section 8.1 (Abdel-Fattah and El-Genk, 1998; Bechtel SAIC Company, LLC, 2003). Colloidal sorption to the air–water interface is thought to be irreversible due to capillary retention present from a net negative change in the interfacial energies (Wan and Wilson, 1994). Colloidal radionuclides irreversibly sorbed onto a mobile air–water interface can move at increased velocities (Abdel-Fattah and El-Genk, 1998). However, if the radionuclides are sorbed to an immobile air–water interface, then transport will be retarded. The retardation of the colloids is dependent on the sorption affinity of the colloids to the interface and the degree of saturation (Bechtel SAIC Company, LLC, 2003).

The Derjaguin, Landau, Verwey and Overbeek theory accurately predicts the sorption behavior of colloids to immobile surfaces only under certain conditions. Positively charged colloids displayed greater affinity to the air–water and glass–water interfaces than negatively charged colloids (Abdel-Fattah and El-Genk, 1998). The increased attraction is likely due to the opposite charges between the colloids and the air–water and glass–water interfaces. In agreement with the Derjaguin, Landau, Verwey and Overbeek theory, increasing the ionic strength of the solution caused a significant increase in the sorption of negatively charged colloids to the air–water and glass–water interfaces (Abdel-Fattah and El-Genk, 1998). The sorption is caused by an increase in the number of ions in solution, which decreases the repulsive electrostatic interactions between colloids of the same charge. Furthermore, sorption of hydrophobic and hydrophilic colloids to the air–water interface was irreversible, caused by the presence of a capillary potential well. However, the presence of the air–water interface in the unsaturated zone produced experimental findings in disagreement with the Derjaguin, Landau, Verwey and Overbeek theory. Despite the anionic charge of both the colloids and interfaces, the colloids sorbed to both the air–water and glass–water interfaces, with higher affinity to the air–water interface (Abdel-Fattah and El-Genk, 1998).

Desorption behavior of colloids from immobile surfaces can also be described in two steps: detachment followed by transport (Kretzschmar, et al., 1999). Desorption tends to occur in the presence of high pH, high sodium saturation, and low ionic strength (Kretzschmar, et al., 1999). Absent solution chemistry and flow rate transients, desorption is negligible, especially in unsaturated media (DeNovio, et al., 2004). For unsaturated conditions, physical or chemical disturbances must occur for desorption of colloids to be significant. The colloid desorption process depends on time and the ionic strength of the solution (McDowell-Boyer, 1992). Desorption of colloids from the rock matrix also occurs as a result of variations in degrees of water saturation (Chen and Flury, 2005). Experimentation showed the highest concentration of colloids released occurred as the system approached saturation (Keller and Sirivithayapakorn, 2004).

### **8.2.1 Factors Affecting Sorption at the Air–Water Interface**

There are several factors affecting the sorption behavior of colloids to the air–water (or air–water–solid) interface. The rate of colloid sorption is greater for unsaturated conditions than for saturated conditions (Keller and Sirivithayapakorn, 2004). This is caused by the increase of air–water interfaces in low water content conditions, which provide more locations for sorption to occur. The extent of sorption of colloids to the air–water interface also increases with the hydrophobicity of the colloid surface (Keller and Sirivithayapakorn, 2004).

Attachment to the air–water interface is dependent on pH, ionic strength, and surface properties of the colloid (DeNovio, et al., 2004). The air–water–solid interface region is particularly important for hydrophilic colloids because repulsion forces between hydrophilic colloids and the gas phase are greater than repulsive forces between the colloid and the solid phase (DeNovio, et al., 2004; Chen and Flury, 2005). This allows the colloid to associate closely with the solid surface as water thickness diminishes, fostering attachment to the solid surface (DeNovio, et al., 2004; Chen and Flury, 2005). Increases in ionic strength increase sorption of colloids to the air–water–solid interface because the magnitude of the repulsive energy barrier between the negatively charged air–water interface and negatively charged colloids is decreased, which promotes colloid sorption (DeNovio, et al., 2004).

### **8.3 Results of Colloid Sorption Experiments**

Chin, et al. (2002) conducted experiments with silica colloids and a glass plate prepared from glass cover slips, representative of a rock matrix, to determine the sorption behavior of colloids. Atomic force microscopy assessed sorption directly. Preparation of a colloidal probe consisted of gluing a 3- $\mu\text{m}$  silica particle to a microfabricated atomic force microscopy cantilever with epoxy. Atomic force microscopy was used to measure the forces between the glass plate and silica colloids in solutions of varying ionic strength (sodium chloride), pH, and copper concentration (copper nitrate). A curve of force versus separation was established by multiplying the tip deflection by the spring constant to obtain the force. With copper ions present, the measured atomic force microscopy forces between the silica particles and the glass plate were strong functions of pH. At low pH values, where no sorption or precipitation of copper occurs, the atomic force microscopy forces present were equal to that without copper in solution. At intermediate pH, a time-dependent surface force was measured with atomic force microscopy. At high pH conducive to precipitation of copper, where removal of silica particles was attributed to precipitation, the force measured between the colloids and the glass plate was the same as without copper present.

Buffered, deionized water mobilized (i.e., desorbed) colloids with the rate of desorption dependent on the flow rate (McDowell-Boyer, 1992). A separate experiment conducted with a 0.05 M NaCl solution and flow rates of 10 or 100 m/d [32 or 320 ft/d] indicated the majority of colloids were detached upon contact with the deionized water, and the rate of desorption was independent of time (McDowell-Boyer, 1992).

When sorption sites of the column materials were saturated with calcium prior to the introduction of low ionic strength solution, low quantities of radionuclides were desorbed (Roy and Dzombak, 1996). Based on previous studies conducted by others, Kretzschmar, et al. (1999) concludes these findings display the stabilizing effect of calcium on colloid release.

Two column experiments using acrylic or glass columns which focused exclusively on colloid desorption and were not conducted subsequent to colloid deposition experiments have also been conducted (Keller and Sirivithayapakorn, 2004; McDowell-Boyer, 1992). Results indicated the highest concentration of colloids released occurred as the system approached 100 percent water saturation (Keller and Sirivithayapakorn, 2004).

## **9 PHYSICAL AND CHEMICAL FACTORS AFFECTING DEPOSITION AND MOBILIZATION OF COLLOIDS**

Contaminant fluxes located within groundwater may be dependent on colloid mobilization (Lenhart and Saiers, 2002). Several factors govern the transport and distribution of colloids in groundwater. These factors include (i) mass-transfer reactions, such as the sorption (and desorption) of colloids to rock surfaces and the sorption of radionuclides to colloids, and the rates of these reactions, (ii) the wetting history of rock and soils in the vadose zone; for instance, are the soils imbibing or drying? (iii) the moisture content of rock in the vadose zone, (iv) pore throat diameters and fracture widths, and (v) the velocity of groundwater (DeNovio, et al., 2004; Lenhart and Saiers, 2002; McCarthy and McKay, 2004; Roy and Dzombak, 1996). Colloidal deposition and release within a porous system is an inherently dynamic process exhibiting variable kinetics during the process that are dependent upon several controlling physical and chemical factors. These factors include chemical surface characteristics of the colloid, solution chemistry, flow intensity, colloid and pore geometry, and pore distribution. The following sections discuss the physical and chemical factors affecting colloid mobility in the subsurface.

### **9.1 Colloid Size and Pore Size Distribution**

The physical size of colloids affects transport by constraining the colloid to preferential flow paths and larger pore networks within a porous matrix (Bradford, et al., 2005, 2002). As mentioned previously, large colloids experience increased physical straining with blocked pores acting as dead ends for colloid migration. However, physical straining is less significant with small colloids (Bradford, et al., 2005). Additionally, dense (heavier than water) colloid suspensions exhibit increased physical straining relative to neutrally buoyant colloid suspensions (Chrysikopoulos and James, 2003). If geochemical heterogeneity exists and anisotropy of the porous matrix is oriented along the flow path, increased colloid spreading and transport will occur along preferential flow paths (Chrysikopoulos and James, 2003; Sun, et al., 2001).

Colloids will likely encounter pores of varying size distribution. The smaller pores promote physical straining, preventing larger colloids from passing through the pore throats (Bradford, et al., 2005). These factors tend to confine the colloid transport paths to larger pore networks and preferential flow paths, where most colloid transport occurs in the hydraulically active network of large pores (Bradford, et al., 2005).

Colloidal straining occurs at pore throats too small in size to allow for the passage of larger colloids and may also occur in unsaturated conditions when colloids encounter thin water films with thicknesses less than the colloid's diameter (Bradford, et al., 2004; DeNovio, et al., 2004; Chen and Flury, 2005). In water unsaturated conditions, attachment of colloids to immobile grain surfaces (also known as blocking) and straining phenomena often occur at the interfaces between the solid grains, water, and air. Factors that enhance retention at these interfaces may include variations in pore water content, motion of colloids within pendular rings (water occupying gaps between grains), and low laminar flow velocities near the grain surface near the interfaces (Bradford, et al., 2004; Crist, et al., 2005). Crist, et al. (2005) observed colloids retained near the air–water–surface interface appeared to become trapped as the perimeter of the meniscus decreased during desaturation. Experiments by Zevi, et al. (2005), utilizing a

bright field microscopy technique to determine the position of water and colloids, identified film straining as having no significant role in the retention of large colloids, but also agreed that interface retention was a major feature, noting that colloids retained at the air–water–meniscus–solid interface had diameters that equaled the film thickness diameters. The experimental findings of Chen and Flury (2005) showed that retention of mineral colloids in sediment-packed columns increased with decreasing saturation, and under constant chemical conditions, colloids retained within the columns can be quantitatively released during resaturation. Chen and Flury (2005) hypothesized this behavior was evidence of colloid retention near the air–water–solid interface. They proposed that repulsive forces associated with approach of hydrophilic colloids toward the water–air interface enabled the colloids to overcome repulsive forces between the colloids and solid near the thin edges of the air–water–solid interfaces and resulted in weak attachment of the colloids to the immobile phase.

As soil grain size decreases, increased colloid deposition occurs (Bradford, et al., 2003; Kessler and Doering, 2000). Larger colloids are removed from the pore water due to enhanced deposition at small pores and also experience pore size exclusion by migrating through single pores with higher velocity (Bradford, et al., 2003; Chen and Flury, 2005; Chen, G., et al., 2005). A recent model developed by Bradford and Bettahar (2006) includes a liberation term in the equation to account for repulsive colloid-colloid interactions. The interactions occur at high colloid concentrations when aqueous phase colloids interact with strained colloids (Bradford and Bettahar, 2006). A table is presented in the publication summarizing the straining, liberation, attachment, and detachment coefficients identified in each experiment conducted.

## **9.2 Ionic Strength, Electrical Charges, and pH Variations**

Similar to the factors affecting colloidal stability, variations in the charge of the porous matrix and colloid surfaces, as well as the electrolyte type and concentration of solutes, are important factors affecting colloid deposition and release kinetics. While particle size affects the extent of colloid transport, solution chemistry appears to be the more dominant factor in colloid transport models (Kessler and Doering, 2000; Kretzschmar, et al., 1999; McCarthy, et al., 2002;). Experiments conducted at fixed ionic strength in a shear zone at the Grimsel Test Site (discussed further in Section 11.2) show the stability of bentonite colloids is strongly dependent on the pH and salinity of the groundwater (Mori, et al., 2003). The surface charge of a porous matrix is strongly influenced by the pH of the solution and the presence of adsorbing ions such as organic polyelectrolytes (Kretzschmar and Sticher, 1998). The presence of natural organic matter adsorbed on mineral surfaces may mask underlying geochemical heterogeneity of a porous matrix (Elimelech, et al., 2000).

Experimental findings suggest an increase in polyelectrolytes (i.e., organic matter) increases colloid mobility, and correspondingly, decreases colloid deposition by approximately two orders of magnitude (Kretzschmar, et al., 1999; Kretzschmar and Sticher, 1998). The presence of organic matter creates a large net surface charge on a particle, which increases the electrostatic repulsion, allowing the particle to become much more resistant to aggregation or attachment (Deshiikan, et al., 1998; Kretzschmar and Sticher, 1998). The negative charge of organic matter in solution is related to solution chemistry and is partly controlled by the presence of carboxyl and phenol groups (Deshiikan, et al., 1998; Franchi and O'Melia, 2003). Greater colloidal particle transport rates may occur because they are more resistant to aggregation or attachment.

Conversely, decreases in the concentration of organic matter may increase the attachment of particles (Deshiikan, et al., 1998). Through experimentation, Kretzschmar, et al. (1998) demonstrate the immobility of pure iron-oxide colloids in negatively charged soils or aquifers composed mainly of quartz, feldspars, layer silicates, or other negatively charged minerals. They also demonstrate how these positively charged colloids tend to be mobile only in strongly acidic, oxide-dominated aquifers with low organic matter (Kretzschmar and Sticher, 1998). Similarly, groundwater environments having iron oxyhydroxides as mineral coatings and low organic material should severely curtail colloid mobility by providing positively charged surface sites for natural colloids, which commonly have negative surface charges (Johnson, et al., 1996). Oxide minerals appear to be the controlling factor in the surface reactivity of dispersed particles and of the soil matrix in highly weathered oxic systems. Soil matrix charge reversal can be associated with even minor changes in cation and anion identity and valence, pH of the solute, and the ionic strength of the solute (Seaman, et al., 1995).

The mobilization of colloids is determined in part by the net interaction potential, which is the sum of the electrical double-layer force, the van der Waals force, and short-range solvation or steric forces (Lenhart and Saiers, 2003). The magnitude and sign of these forces is dependent on the physical and chemical characteristics of the mineral and colloid surfaces. The mass of colloids available for detachment and mobilization varies directly with the magnitude of ionic strength transients and other variations in groundwater chemistry that induce changes in the net interaction potential (Lenhart and Saiers, 2003). Additionally, weathering processes can produce large quantities of secondary colloid-sized minerals that can become mobilized during rain events (Laegdsmand, et al., 1999; Ryan and Elimelech, 1996).

Consistent with impacts on colloid stability discussed in Section 5, variations in ionic strength also affect the electrostatic interaction between colloids and soil grains. Field and laboratory column experiments were conducted in which the effects of ionic strength (measured by specific conductance) and pH on colloid mobilization were measured (Bunn, et al., 2002). Bunn, et al. (2002) noted that colloid releases in the subsurface were associated with changes in pH (in this case, an increase in pH from ~6 to greater than 10), but also noted few colloids were released in field tests as a result of only lowering ionic strength. At very high pH values (~13.1), increased ionic strength caused by the pH increase reduced the electrostatic repulsion and reduced the quantity of colloids released (Bunn, et al., 2002). In experiments conducted using glass columns, Kretzschmar, et al., (1997) showed that at low ionic strength, the colloid deposition rate increases greatly and is only limited by the frequency of colloid–matrix collisions. Experiments conducted using Yucca Mountain tuff have also indicated a greater fraction of colloids is deposited as ionic strength is increased, and this increased deposition can be modeled as a pseudo-first-order process (Kessler, 1999). In contrast to nearly all other studies, the results of Roy and Dzombak (1996), using two columns packed with natural porous media and one column packed with idealized glass beads, showed an increase in colloid mobilization at lower ionic strength as measured by interaction potential energy profiles that showed colloid detachment.

The repulsive energy barrier controls the surface area available for a colloid–surface interaction (Johnson and Elimelech, 1995). If a repulsive energy barrier between colloids and a hydrophilic surface is absent, aggregation of the colloids will be favored (Crist, et al., 2005). Rapid aggregation of colloids will force new particles to immediately attach at the periphery of existing aggregates. This is presumably the most significant mechanism of hydrophobic colloid retention (Crist, et al., 2005). Weronki, et al. (2003) showed that secondary energy wells

(deposition) may be produced by depletion of attraction forces and that a fraction of colloids may undergo slower transport than the bulk transport. A bimodal shape observed in the breakthrough curves during low flow velocities suggests two pathways exist for particle transport—a rapid transport pathway and a slower transport rate associated with secondary energy well(s) (Weronski, et al., 2003). The secondary energy wells and surface charge heterogeneities were identified as contributing factors for the deviation of the colloid filtration theory (Tufenkji and Elimelech, 2005).

Experiments investigating the relationship between pH and colloidal deposition have produced conflicting interpretations of results. Some investigators have concluded that the deposition efficiency of colloids is determined by the pH of the solution (Bunn, et al., 2002; Roy and Dzombak, 1997), while others (Gao, et al., 2004; Ryan and Gschwend, 1994) have concluded that clay colloid deposition is more strongly dependent on the mineralogy of the colloid than the effects of solution pH. These investigators identified differences in the deposition of differing clay colloids with similar variations of pH. For instance, the deposition rates of illite colloids, under steady-flow conditions, were essentially independent of the pH, but the deposition of kaolinite colloids nearly doubled when the pH was decreased from 7.4 to 4.6 (Ryan and Gschwend, 1994). Given these conflicting interpretations, additional experimentation may be warranted to determine the relationship between pH and colloidal deposition.

### **9.3 Pore Water Velocity**

Pore water velocity is an additional physical factor controlling transport rates and quantities of colloids. Pore water velocity is associated with several physical factors found within experimental media and natural rock settings. Kretzschmar and Sticher (1998) showed colloid deposition rate coefficients are functions of pore water velocity, but that pore water velocity had only a minor effect on the first-order kinetic deposition when humic material was present. Electrostatic attraction and specific adsorption via ligand exchange bind humic matter to oxide surfaces and clay mineral edges (Kretzschmar and Sticher, 1998). This results in charge neutralization and destabilization of oxide particles, so that at low to moderate flow velocities, the deposition rate of the particles increases with flow velocity (Kretzschmar and Sticher, 1998). This behavior was also measured in studies of columns packed with sand. An experiment by Noack, et al. (2000) identified colloid breakthrough curves as sigmoidal in nature, implying colloids experience hydrodynamic dispersion, convection, and diffusion. Grolimund, et al. (1998) showed that the dispersivity of colloids was essentially independent of pore water velocity. During convection, colloids are transported by mass flow through large pores, but due to diffusion limitations, colloids will follow concentration gradients established by convective flow (Noack, et al., 2000).

Using columns packed with minimally disturbed soil samples, Laegdsmand, et al. (1999) showed colloid mobilization varied with rates of simulated rainfall infiltration and with length of time of the infiltration event. Columns in the experiments were allowed to drain after each simulated rainfall. For initial colloid releases, organic matter-rich colloids dominated, but ionic strength began to be the controlling factor with continued rainfall simulations. During long-term rainfall simulation, ionic strength became a less controlling factor and diffusion in the matrix or across the water stream and the macropore wall became the controlling mechanism for colloid release (Laegdsmand, et al., 1999).

A field-scale study on colloid migration by McKay, et al. (2000) suggests that retention of colloids is not uniform in heterogeneous material because measured rates of the decline of colloid tracer concentrations varied with distance (i.e., the “tails” of the colloid breakthrough curves had differing decay rates and varied with distance). Reappearance of colloid tracers occurred 1 to 5 months after the initial pulse had passed and generally corresponded to increased seasonal precipitation (McKay, et al., 2000).

## **9.4 Representing Colloid Deposition and Mobilization**

In addition to the physical and chemical factors controlling colloid transport, detachment and attachment kinetics can be used to describe how colloids are released from and deposited on the porous matrix or fracture surfaces. The kinetics involved in detachment and attachment are related to physical and chemical conditions of the host rock and pore water. Van de Weerd, et al. (1998) stress that the kinetics of colloid attachment to and detachment from the solid matrix and transfer of contaminants between the solid matrix and mobile and immobile colloids may be time dependent and nonlinear, especially when comparing contaminated to noncontaminated situations. Grolimund, et al. (2001a) suggest that colloid release cannot be described by a single population released according to a first-order kinetic rate law.

Attachment kinetics are controlled by the rate of transport to a solid surface and subsequent attachment to that surface. The kinetics involved are described as a colloid retention mechanism involving collision and fixation of the colloids to a porous medium (Bradford, et al., 2005). However, Bradford, et al. (2002) state the current filtration theory does not adequately predict the fitted first-order attachment coefficients, likely due to straining, as the primary mechanism for colloid removal. Others also found that the filtration theory did not agree with first-order attachment, and straining could be a significant factor of colloid deposition (Li, et al., 2004).

Upon deposition to a surface, most colloids will remain attached to that surface, and the attachment is often described and modeled as a kinetic process (Johnson, et al., 1996). Lenhart and Saiers (2002) discuss how single rate law formulations do not fully describe mass transfer kinetics, and argue that a dual rate law, which includes a first-order rate law to simulate film straining and a second-order rate law to simulate capture at the air–water interfaces, provides a better model for colloid mobilization and transport in the unsaturated zone of porous media (Cherrey, et al., 2003; Lenhart and Saiers, 2002).

In an experimental and modeling study of the effects of chemical transients on colloid retention and mobilization, Lenhart and Saiers (2003) successfully modeled the mobilization of silica colloids due to changes (reductions) in pore water NaCl concentrations. Lenhart and Saiers (2003) conceptualized multiple groups or compartments within the attached colloid population and modeled release by assigning a critical release concentration to each group based on a linear distribution function. Consistent with the experimental data, simulated NaCl perturbations succeeded in mobilizing nearly all of the colloids retained within the compartments (Lenhart and Saiers, 2003). Additionally, at the onset of the first chemical perturbation, the release rate of the colloids was 37 times greater than the time scale for advective transport, but under steady state conditions, the energy barrier remained and inhibited colloid release. Lenhart and Saiers (2003)



concluded that successful quantification of colloid mobilization depends upon an accurate description of temporal variability in NaCl concentration. Additionally, the rate of colloid release is not a simple linear function, but rather is represented by a multicompartment linear-kinetics model which replicates colloid mobilization more accurately (Lenhart and Saiers, 2003).

## 10 EXPERIMENTAL AND MATHEMATICAL MODELING OF COLLOIDAL TRANSPORT

Numerous studies have been published that utilize physical models (e.g., packed columns) under controlled situations to investigate colloid transport. In these studies, colloids of various sizes and compositions are typically injected into columns containing unconsolidated sediment or fractured rock, and components such as solution ionic strength, solution pH, degree of saturation, flow velocity, and soil matrix are varied. Breakthrough curves are often developed from the studies, which also measure concentrations of conservative tracers (e.g., bromide or tritium) and colloids recovered in the outflow. The concentration and/or particle size distribution of colloids recovered can be compared with the number of colloids injected to quantify important processes (e.g., straining, blocking, filtering and mobilization) affecting colloidal transport. These experiments provide a real data set for which numerical models can be developed and employed to fit data and offer insight into colloidal transport mechanisms. A brief summary of some of the more recent studies is provided in this section.

Several experimental and numerical modeling studies within the published literature specifically investigate the transport of colloids through fractures and alluvium at Yucca Mountain. These studies are also briefly addressed in the following paragraphs.

### 10.1 Experiments and Modeling of Conditions Directly Relevant to Yucca Mountain

Kersting, et al. (1999) identified and examined groundwater from the Nevada Test Site that contained measurable quantities of plutonium, associated with colloid-sized particles, which apparently traveled over 1.3 km [0.81 mi] over a period of about 30 years. This study, perhaps more than any other, highlighted the potential for colloid-facilitated transport of low solubility and highly sorbing radionuclides such as plutonium. The Nevada Test Site is adjacent to Yucca Mountain and shares many similar climatic and geologic characteristics with the region surrounding the potential repository. Several additional factors beyond groundwater transport may have facilitated the transport of plutonium recorded by Kersting, et al. (1999) including gaseous transport through fractures in volcanic tuffs. Subsequent studies, however, generally confirm the transport of plutonium via groundwater (Allen, et al., 2003).

Two publications by Gamerding and Kaplan (2001a,b) compare the effects of water saturation and ionic strength on colloid-sized particles migrating through quartz sand and Yucca Mountain tuff material. The major differences identified between the sand and tuff used in the experiments were the physical characteristics of the grains (e.g., roundness of the sand versus the angularity of the tuff material). The concentration of colloids was determined using fluorescence spectroscopy (Model L550B luminescent spectrophotometer, Perkin-Elmer Corporation, Norwalk, Connecticut) (Gamerding and Kaplan, 2001a). For the experiment conducted under unsaturated conditions, a centrifuge method (Model L8-UFA, Beckman Coulter, Inc., Fullerton, California) was utilized to drive colloid transport. The colloid analogs used in these studies were carboxyl-modified polystyrene latex microspheres (Gamerding and Kaplan, 2001a,b).

The unsaturated experiment conducted by Gamerdinger and Kaplan (2001b) compared the effects of varying ionic strength of solutions and the degree of saturation on the deposition of colloids in the experimental columns. Results of experiments conducted at ionic strengths comparable to that of Yucca Mountain groundwaters indicated that the combined effects of some physical and chemical processes were synergistic and produced greater colloid deposition. At the maximum saturation and minimum ionic strength studied, the combined effects of physical and chemical processes produced greater colloid mobility. As ionic strength increased and degree of saturation decreased, greater colloid deposition occurred. For unsaturated conditions at high degrees of saturation (i.e., greater than 28 percent for sand and 66 percent for tuff), colloid recovery was greater than 100 percent, indicating no retention of colloids. This finding was interpreted to be in agreement with the Derjaguin, Landau, Verwey and Overbeek theory (Gamerdinger and Kaplan, 2001b).

Results of the experiment conducted under saturated conditions were presented as breakthrough curves depicting the dimensionless effluent concentration as a function of cumulative pore volumes eluted (Gamerdinger and Kaplan, 2001a). Colloid deposition was modeled as an irreversible process, with a retardation factor based on the velocity of the colloids through the column. The retardation factor is typically used to quantify the process of sorption, which according to the investigators is relatively unimportant when compared to deposition (filtration) (Gamerdinger and Kaplan, 2001a). Experimental findings indicated colloid transport in saturated conditions within the Yucca Mountain tuff is limited by the ionic strength of the pore water. Additionally, it was determined that solution chemistry, not the physical properties of the grains, is the controlling factor in colloid deposition (Gamerdinger and Kaplan, 2001a). This agrees with the findings of others (Crist, et al., 2005; Bunn, et al., 2002; Roy and Dzombak, 1997), but disagrees with Bradford, et al. (2005), who postulated that physical straining was the most dominant colloid retention mechanism in porous material.

The Electric Power Research Institute also conducted an experiment on colloid transport and deposition under saturated and unsaturated conditions relevant to Yucca Mountain (Kessler, 1999). Experiments were conducted utilizing water chemistries resembling those predicted during near- to long-term high level nuclear waste storage at Yucca Mountain and porous media representing Yucca Mountain tuffs (Kessler, 1999). Specific equipment utilized to model saturated conditions included glass columns (Kontes, Vineland, New Jersey) with an inner diameter of 2.5 cm [1 in] and an infusion pump to maintain saturated conditions and inject the colloid and tracer solutions. The column system for unsaturated conditions included two infusion pumps and an L8-UFA, an Unsaturated Flow Apparatus (Beckman Coulter, Inc., Fullerton, California). Results showed that solution chemistry is a dominant factor in colloid mobility, which is substantially reduced by increasing the ionic strength by a factor of 10 or by decreasing the water saturation to less than 20 percent. However, reduced saturation had little effect on colloid transport at high ionic strength where deposition was likely from coagulation (Kessler, 1999).

Contardi, et al. (2001) prepared a Yucca Mountain site-specific simulation for transport of radionuclides sorbed onto colloids using the NRC TPA Version 3.2 code. For a compliance period of 10,000 years, the model simulation predicted that plutonium and americium colloidal transport contributed less than 0.1 mrem/yr peak mean total effective dose equivalent, but the results were strongly dependent on assumptions regarding container life (Contardi, et al., 2001).

A three-dimensional site-scale numerical simulation of radioactive colloid transport at Yucca Mountain utilized true colloids with properties of  $\text{PuO}_2$  and radioactive decay characteristics of Pu-239 (Moridis, et al., 2003a). Four different colloid sizes {6, 100, 200, and 400 nm [ $2.4 \times 10^{-4}$ ,  $4 \times 10^{-3}$ ,  $8 \times 10^{-3}$ , and  $1.6 \times 10^{-2}$  mil]} were modeled in four different simulation cases. The first case modeled assumed no declogging of pore throats occurs and once filtered, colloids did not detach from the pore/fracture walls. The second case assumed a strong kinetic declogging force and was postulated to represent a maximum colloid transport scenario. The third case assumed a weak kinetic-based declogging force and represented a mild equilibrium filtration scenario. The final case presented a scenario where no declogging occurred but in which fractures were assumed to have transport properties of the surrounding matrix (Moridis, et al., 2003a). At the time of publication (2003), no information existed on the kinetic declogging coefficient incorporated into Moridis' model. The declogging coefficient was treated as a fraction of the forward kinetic coefficient to maintain dependence on the flow velocity. Moridis, et al. (2003a) concluded that the transport of colloids in the unsaturated zone at Yucca Mountain is strongly influenced by the kinetic declogging coefficient based on results of simulations with a declogging coefficient of zero in which no colloids reached the water table. Small non-zero values of the declogging coefficient produced long travel times to the water table (12,000 years to infinity) in the simulations, and large values of the declogging coefficient resulted in rapid transport times to the water table (15–30 years). Moridis, et al. (2003a) noted the need for further research regarding the declogging coefficient due to the extreme sensitivity of the coefficient and dearth of information currently available on the subject.

Additional numerical modeling of colloidal transport in the unsaturated zone at Yucca Mountain highlights the importance of considering daughter isotopes in the transport of highly sorbing radionuclides such as plutonium (Moridis, et al., 2003b). Model results indicated the differing transport and sorption characteristics of immediate daughters, such as the U-235 daughter of Pu-239, significantly affected predictions of which nuclides were important after long simulation periods. For example, in these simulations, U-235 reached the water table first and was the dominant radionuclide based on mass fraction released after 2,000 years (Moridis, et al., 2003b).

DOE prepared a report on colloid formation and its potential effects on radionuclide transport at Yucca Mountain (DOE, 2002). The report presents several ongoing studies of analog sites in the United States and abroad, comparing field and laboratory studies. Additionally, a conceptual model for colloid formation and transport is presented in schematic form and a literature review of applicable research is provided within the report.

## **10.2 Colloid Transport in Fractures**

Although the groundwater velocities in fractured media are well-described by Darcy's law, the apparent velocities of colloids exceed those predicted by Darcy's law (Pudewills, et al., 2002; Baek and Pitt, 1996). One numerical simulation incorporated a three-phase system to develop a full-equilibrium model (Baek and Pitt, 1996). The retardation coefficient, the hydrodynamic dispersion coefficient, and the fracture width were varied to examine the resulting equilibrium distribution coefficient of a colloid with a sorbed radionuclide. This model predicted faster transport rates of colloids due to limited diffusion of colloids into the rock matrix. Modeling by Oswald and Ibaraki (2001) concluded that diffusion of colloids from fractures into a porous matrix occurs and can significantly retard the migration rates of colloids within fractures. A field

experiment by Gwo, et al. (2005) showed that advection dominates matrix diffusion, and diffusion is likely to be confined only to the preferential flow path in a fracture system.

In addition to the batch experiments conducted by Mori, et al. (2003) discussed previously, *in situ* experiments at the Grimsel Test Site were carried out in a fully characterized shear zone on the migration of radionuclides and the influence of smectitic-bentonite colloids on transport in fractures (Mori, et al., 2003). In the experiment, colloids were observed under a quasi-static condition, suggesting colloids may be produced without the aid of mechanical forces. However, the colloidal and total solid fraction observed at the shear zone interface did increase with water flow. Ryan, et al. (1998) showed that rainfall events increase the mobilization of colloid-sized particles in fractures in soils. However, a time period of recovery for processes that generate colloids must occur slowly between rainfall events (Ryan, et al., 1998).

The experimental findings of Mori, et al. (2003) showed that bentonite colloids significantly influence the *in-situ* retardation behavior of trivalent and tetravalent actinides. Also, depending on the advective flow rate of the groundwater, bentonite colloids can form at bentonite and host rock interfaces with the colloidal stability strongly dependent on the pH and salinity of the groundwater. Migration behavior and transport of americium and plutonium were strongly influenced by bentonite colloids and was faster than the transport of dissolved species in the groundwater. With bentonite colloids present, 60–80 percent recovery of americium and plutonium was recorded; however, in the absence of bentonite colloids, only 20–30 percent recovery was noted (Mori, et al., 2003).

Additional studies regarding radionuclide and colloid transport in a shear zone of the Grimsel Test Site indicated a minor influence of diffusive processes on the transport of colloids (Kosakowski, 2004). The experiment consisted of several boreholes, used as injection and extraction wells, drilled into the planar experimental shear zone. The breakthrough curves of uranine (a nonsorbing solute) and bentonite colloids were studied because the curves are highly reproducible and measurements are not biased by temporal changes of the hydraulic boundary conditions. The experimental findings demonstrated that models based on the advection-dispersion equation and matrix diffusion (Fickian representation) do not adequately describe the temporal and spatial evolution of colloid transport. Two different models were evaluated: the advection–dispersion (matrix diffusion) model and the non-Fickian dispersion (Continuous Time Random Walk) model. The effective diffusion coefficient in a porous medium was identified from the models. The coefficient depends on the structure of the pore space—it is lower than in a free water system by a factor of between 0.01 (clay) and 0.7 (sand), and the effective matrix diffusion coefficient for the smallest measured colloid size was below  $1.7 \times 10^{-13} \text{ m}^2/\text{s}$  [ $1.8 \times 10^{-12} \text{ ft}^2/\text{s}$ ]. The experiments concluded that diffusive processes have only a minor influence on the transport of colloids in the shear zone. This conclusion was determined by comparing measured breakthrough curves with a calculated curve adjusted using a higher pore diffusion coefficient (corresponding to a smaller colloid). The calculated curve showed a distinct shift where the measured curves showed no shift. If diffusion processes were significant, the measured curve would have shown a shift (Kosakowski, 2004).

Prior to the work performed by Kosakowski (2004), James and Chrysikopoulos (1999) modeled polydisperse colloid transport in a single fracture. The model is a particle tracking model for flow in a uniform fracture, which can be idealized as Poiseuille flow with particles being both advected along the velocity gradient and dispersed due to molecular diffusion. Particle tracking is the only method that can facilitate variably sized colloids. Because each particle is

individually considered and colloid deposition onto fracture surfaces is considered a relatively fast process, the sorption relationship of Smulochowski-Levich is valid (James and Chrysikopoulos, 1999). The Smulochowski-Levich relationship describes deposition onto sorbent surfaces as a function of colloid concentration, flow velocity, molecular diffusion coefficient, fracture aperture, and distance from fracture inlet, and also assumes particle wall hydrodynamic repulsive interactions are counterbalanced by van der Waals attractive forces. The investigation by James and Chrysikopoulos (1999) found that polydisperse colloid suspensions and monodisperse suspensions exhibit different transport characteristics. Polydisperse colloid plume spreading is proportional to the variance of the colloid diameter distribution, and small colloids have a large molecular diffusion coefficient while large colloids have a large Taylor dispersion coefficient. This allows large colloids to arrive earlier than smaller colloids due to greater dispersion. Colloid plumes with a greater variance in individual colloid diameter will become progressively more retarded from the increased concentration of small colloids trapped in the solid matrix. This is due to the slower average velocity of small colloids and their preferential diffusion into the solid matrix. Additionally, the models displayed an inversely proportional relationship of particle sorption to the fracture aperture, and substantially different colloid distributions may be encountered when the fracture surface area is relatively large (James and Chrysikopoulos, 1999).

Li, X., et al. (2004) and Li, S., et al. (2004) conducted a modeling analysis that considered colloid sorption onto fracture surfaces, diffusion into rock matrix, and reversible sorption on the rock matrix. Their modeling approach incorporated a fully implicit, finite difference method that employed a two-point backward difference approximation in time (known as the Euler implicit scheme), a central difference approximation for the second derivative in the spatial coordinate, and an upwind difference approximation for the first derivative in the spatial coordinate. Model results indicated the concentration of mobile colloids in fractures was sensitive to the filtration coefficient for colloids and the matrix diffusion flux of colloids (Li, S., et al., 2004).

Chrysikopoulos and Abdel-Salam (1997) modeled colloid transport and deposition in saturated fractures with spatially variable apertures. The results demonstrate the influence previously deposited colloids have on additional colloid deposition and showed that colloid retention could be described by a linear or a nonlinear dynamic blocking function. The model accounted for size and surface exclusion, but not diffusion. The nonlinear blocking function predicted much greater liquid-phase colloid concentrations (i.e., less colloids retained) than would be estimated when assuming continuously "clean" media for the retention of colloids. However, the effect of higher liquid-phase colloid concentrations, which limit the retention of colloids due to surface exclusion effects, becomes insignificant at high reverse rate coefficients (Chrysikopoulos and Abdel-Salam, 1997).

A multiscale approach was developed by Kulkarni, et al. (2005) to predict multiple layer irreversible colloidal deposition in the presence of interparticle electrostatic and van der Waals interactions. The computational method incorporates kinetic information obtained from mesoscopic stochastic simulations of particle deposition using a macroscopic conservation equation for colloidal transport. In the analysis, a sequential algorithm was utilized that released particles singularly. A new particle would only be released into the simulation after the previously released particle had been deposited. The algorithm would track the total deposition time required by each particle but could not provide an actual, chronological time scale for deposition. However, this method was capable of extracting transient features of deposition dynamics relating to particle deposition (Kulkarni, et al., 2005).

Marseguerra, et al. (2001a) presented a model that is an extension of the stochastic model, based on the Kolmogorov-Dmitriev theory and is capable of explicitly quantifying individual interactions that are possibly nonlinear and not at equilibrium. A Monte Carlo method was devised to account for the nonlinearities in the presence of colloids. The Monte Carlo method utilizes a stochastic modeling strategy that selects a large number of particles of solute and then evaluates each selection on the basis of physical validity and probability distribution. This is thought to be an extremely advantageous alternative to applying averaged values (Chen, J., et al., 2005; Marseguerra, et al., 2001a). Another computation utilizing the Monte Carlo method analyzed a case study of Pu-239 transport at a potential high-level waste deposit at Mol, Belgium (Marseguerra, et al., 2001b). The model attempted to predict plutonium transport on a spatial domain of 10 km [6.2 mi] over a timeframe of  $10^4$  years. Results of the modeling showed that the Monte Carlo approach is suitable for propagating the uncertainties that exist in input parameters (Marseguerra, et al., 2001b).

### **10.3 Additional Techniques for Quantification of Colloid Transport**

The quantification of colloidal transport has been primarily studied through column experiments. Transport properties such as retardation factors, dispersion, and diffusion coefficients are typically inferred from breakthrough curves and/or destructive procedures conducted at the end of the experiment (Weisbrod, et al., 2003). Some novel nondestructive methods identified in the literature reviewed are discussed in the following paragraphs.

Weisbrod, et al. (2003) presented a unique methodology for quantification of fluorescent microsphere transport using a controlled wavelength of transmitted light. The light is used to induce a measurable fluorescence from the microspheres, where the fluorescence is separated from the overall light output and corrected for spatial intensity variations to quantify the spatial and temporal distribution of microspheres. However, in this method, Weisbrod, et al. (2003) caution that “a nonlinear link between the degree of saturation and the emission of fluorescent colloids prevents accurate determination of colloid concentration.” However, the technique appears to be useful for determining the transport processes, spatial structures, and the kinetics of colloid transport within a matrix.

Kretzschmar, et al. (1997) also utilized fluorescence and UV-VIS spectrophotometers with a chromatographic short-pulse technique to measure colloid breakthrough curves and colloid deposition rate coefficients. Measurements with the short-pulse technique allowed a fast and accurate determination of colloid deposition rate coefficients under saturated flow conditions (Kretzschmar, et al., 1997).

Grolimund, et al. (2001b) suggested that dynamic light scattering is an efficient method of quantifying colloid deposition and aggregation. Two techniques were compared in experiments: (i) the pulse column technique, which measures deposition kinetics and (ii) dynamic light scattering, which measures particle aggregation kinetics. The data obtained by these two different methods are quite similar. Dynamic light scattering measurements produce kinetic deposition data more quickly than the pulse column technique and can be used to study the influence of various chemical parameters on particle deposition kinetics (Grolimund, et al., 2001b). Critical concentrations for colloid coagulation have also been measured using dynamic light scattering, which is the preferred method because it does not depend on specific experimental conditions. Critical coagulation concentration is the electrolyte concentration at

which the repulsive interaction energy falls below the kinetic energy of an individual particle, thus inducing aggregation of colloids (Czigany, et al., 2005).

Xu, et al. (1997) utilized a nondestructive Kossel diffraction technique to characterize the colloid structure resulting from interparticle interactions in colloid dispersions. The technique is based upon the principles of back light scattering, and it achieved good quantitative agreement between experimental data and theoretical predictions. The equipment utilizes a collimated green light beam {50  $\mu\text{m}$  [2 mils] in diameter and a wavelength of 543 nm [5,430  $\text{\AA}$ ]} produced by a 0.5-MW helium-neon laser (Model 155A, Spectra Physics Laser Products) that is scattered by colloidal particles. This produces a scattering image on the surface of a glass vial where the image intensity is captured by a vertically polarized CCD digital camera (Lynxx 2000 Frame 336\*244FT, Spectra Source Instruments) and downloaded to a computer. The recorded image is then transformed into an intensity profile by image analyzer software (Spectra Source Instruments, Lynxx 2000, Version 3.04b) (Xu, et al., 1997).



## 11 RECOMMENDATIONS

During the literature review, several areas of research were identified in which additional experimentation or modeling could potentially be conducted to improve understanding of colloid-facilitated radionuclide transport. Some of the subject areas include those in which conflicting conclusions were drawn from similar experiments and topics where insufficient information is available from which to draw firm conclusions. Potential experiments and topics for additional study that might aid in refinement of existing colloid transport models follow.

Colloid breakthroughs in experiments conducted under saturated conditions consistently show that at least a small portion of the colloid population travels at or slightly greater than the average flow velocity. Because the relative concentrations of colloids measured as part of the breakthrough are small compared to estimates or measurements of source concentrations, most of the colloids are thought to be sorbed or filtered during transport (Allen, et al., 2003). It has been suggested that there may be multiple distributions of colloid filtration and retardation properties within a given natural colloid population and that use of a continuous single population probability distribution for colloid retardation is not a realistic representation of the small population of early breakthrough colloids (Bechtel SAIC Company, LLC, 2004; Allen, et al., 2003). Column experiments could be conducted to evaluate the nature of early colloid breakthrough and to determine if recently developed multiple rate models (e.g., Cvetkovic, et al., 2004) can be effectively applied to colloid transport behavior.

Batch sorption/desorption experiments could be conducted to determine (i) the extent of the irreversibility of radionuclide sorption to colloids; (ii) the competing effects of dissolved radionuclide sorption to colloid and immobile surfaces (e.g., fracture surfaces, engineered components, and unconsolidated sediment); and (iii) the extent (magnitude) of colloid sorption of radionuclides in complex solutions, in which multiple radionuclides may compete for the colloid surfaces. The colloids used in these studies should be consistent with colloids collected from Yucca Mountain groundwaters and should be of the appropriate size range {~100–200 nm [ $\sim 4\text{--}8 \times 10^{-3}$  mil] average size} (Allen, et al., 2003). The experimental methods used and discussed by Lu, et al. (2000, 1998, 1997), Allen, et al. (2003), and Runde, et al. (2002) could effectively be employed to demonstrate colloid sorption and reversibility and use relatively simple experimental apparatuses and equipment.

The competing effects of calcium and other species in solution may need to be investigated further. Increases in solution ionic strength tend to increase the deposition (sorption and filtration of colloids due to instability and neutralization of surface charge) of colloids but also tend to promote desorption of radionuclides or other species that may be attached to the colloid. The sensitivity of colloid deposition behavior to calcium concentration has been noted (Kretzschmar, et al., 1997), and calcium concentrations in groundwater at Yucca Mountain vary within the sensitive range. Lu and Mason (2001) reported the desorption of strontium from clay colloids (probably due to ion exchange processes) as a result of competition with dissolved calcium and sodium present in J-13 groundwater, and Puls and Powell (1992) noted an increased stability of iron oxide colloids, even at pH values near the pH of zero-point of charge, and subsequent transport of those colloids when phosphates and other species were attached to the colloid surfaces. These effects could be evaluated in experiments similar to those conducted to assess colloid sorption capacity.

Colloids are most often released as a result of chemical or physical transients in the groundwater system. The thermal alteration pulse associated with waste disposal can potentially generate a significant transient in the near-field and unsaturated zone that may increase the availability and transport of colloids. Alteration of host rock may also generate an additional source of colloids in the near field. The timing, magnitude, and nature of potential colloids produced by near-field thermohydrologic transients should be evaluated. If there is a potential for generation of colloids of a different type than those currently sampled from Yucca Mountain groundwaters, these should also be considered for inclusion in sorption characterization experiments (Kersting, et al., 1999; Allen, et al., 2003). Colloids sampled from the unsaturated zone may need to be examined for consistency with those sampled from the saturated zone to ensure naturally occurring colloids are adequately considered in analyses of colloid-facilitated transport (Kersting, et al., 1999).

Several studies have confirmed that increases in ionic strength tend to reduce the stability of colloids and promote colloid sorption or deposition (Kessler, 1999; Bunn, et al., 2002; Kretzschmar, et al., 1997; Roy and Dzombak, 1996). However, the potential for mobilization or remobilization of sorbed or deposited colloids appears to be dependent on the specific conditions of the groundwater and the type of colloid (Bunn, et al., 2002; Roy and Dzombak, 1996). The potential for Yucca Mountain colloids to be mobilized as a result of changes in ionic strength may be considered to address whether deposition in the near-field and unsaturated zone as a result of potential high ionic strength excursions early in the repository postclosure period need to be considered in assessment of colloid-facilitated radionuclide transport.

Similarly, studies of the effects of solution pH on colloid deposition and mobilization have produced differing conclusions. Some studies suggest the effects of solution pH are dominant (Roy and Dzombak, 1997; Bunn, et al., 2002), while others suggest the colloid type is most important (Gao, et al., 2004). Gao, et al. (2004) infer from a study comparing the effects of pH on kaolinite and illite colloids under unsaturated conditions that the mineralogy of the clay is the most important control on colloid deposition and that perturbations in flow are critical in mobilizing vadose zone colloids. The effects of solution pH and variations in natural colloid mineralogy could be examined using porous material (e.g., Yucca Mountain tuff) and experimental procedures similar to Gao, et al. (2004) or Ryan and Gschwend (1994).

There are some discrepancies among results of experiments investigating colloid retention in unsaturated media. The relative importance of film straining and accumulation at the air–water–solid interface varies depending on the type and sizes of colloids used in the studies (e.g., Zevi, et al., 2005; Bradford, et al., 2004; DeNovio, et al., 2004; and Chen, G., et al., 2005). Several novel optical inspection methods have been used to observe and quantify colloid behavior in these unsaturated systems (e.g., Zevi, et al., 2005); however, many of these techniques require the use of colloid sizes that are large {800–4,500 nm [ $3 \times 10^{-2}$  to  $1.8 \times 10^{-1}$  mil]} compared to the expected average colloid size {100 nm [ $4 \times 10^{-3}$  mil]} in Yucca Mountain groundwaters. Additional experiments could help to determine the nature of colloid retention in the unsaturated zone; however, several studies suggest that flow perturbations and changes in saturation have a significant effect on colloid mobilization in unsaturated rocks and sediments (e.g., Gao, et al., 2004). Since the mechanisms of colloid retention by film straining and collection at the air–water–solid interface do not appear to be long-term sequesters of colloids, additional experiments on this topic are of lower priority.

Modeling of colloidal transport indicates some sensitivity to assumptions regarding the rates and nature (e.g., anion and size exclusion) of colloid diffusion into rock matrix. Field and modeling studies reported diffusion is likely to be confined to preferential flow path(s) in a fracture system (Gwo, et al., 2005). Slower or faster colloid transport rates are predicted based on assumptions of anion exclusion (Baek and Pitt, 1996) or substantive matrix diffusion (Oswald and Ibaraki, 2001). Given the uncertainties in quantifying matrix diffusion for dissolved species, experiments to investigate the diffusion properties of Yucca Mountain colloids are recommended.

## **11.1 Experimental Apparatus**

A substantial number of studies have successfully employed the use of flow-through fluorescence and UV-VIS spectrophotometers to quantitatively measure colloid concentrations. Colloids measured using these methods have various compositions (e.g., clays, silica, iron oxides), although carboxylate-modified latex microspheres are most efficiently measured using fluorescence spectroscopy. Other instruments, such as laser diffraction particle size analyzers and spectrometers effectively determine colloid size distributions, especially in the range expected for natural system colloids, but generally require concentrations larger than expected to quantify the number of particles.

Determination and prioritization of experiments to be conducted and equipment required to support those experiments must be informed by the potential risk of the processes examined and program resources available. Other considerations include the potential for collection, analysis, and interpretation of experimental data in time for the data to directly contribute to tools that may be used in reviewing a potential license application and the likelihood of maintaining a long-running experiment through the potential licensing period. To that end, it appears that evaluation of source term uncertainties, such as colloid sorption capacities and competition of radionuclides for colloid sorption sites, as well as the effects of solution chemistry on radionuclide sorption onto colloids and colloid sorption onto rock and engineered materials should be the focus of early experiments.

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