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Technical Basis Document No. 8: Colloids

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Prepared for:
U.S. Department of Energy
Office of Civilian Radioactive Waste Management
Office of Repository Development
P.O. Box 364629
North Las Vegas, Nevada 89036-8629

Prepared by:
Bechtel SAIC Company, LLC
1180 Town Center Drive
Las Vegas, Nevada 89144

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ACRONYMS

AIN	additional information needed
AMR	Analysis and Model Report
CML	carboxylate-modified polystyrene latex
CSNF	commercial spent nuclear fuel
DOE	U.S. Department of Energy
DSNF	DOE spent nuclear fuel
ENFE	Engineered and Near Field Environment
FEP	feature, event, or process
GEN	general agreement
GRS	Gesellschaft für Anlagen und Reaktorsicherheit
HLW	high-level radioactive waste
KTI	Key Technical Issue
LA	license application
NRC	U.S. Nuclear Regulatory Commission
RT	Radionuclide Transport
TSPA	total system performance assessment
TSPAI	Total System Performance Assessment and Integration
TSPA-LA	total system performance assessment for the license application
YMP	Yucca Mountain Project

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1. INTRODUCTION

This technical basis document provides a summary of the conceptual understanding relevant to the projected behavior of radionuclides potentially attached to colloids as they are transported through the engineered and natural features of the Yucca Mountain repository system. This is one in a series of technical basis documents that are being prepared for the different components relevant to predicting the likely postclosure performance of the Yucca Mountain repository. The relationship of colloid formation, stability, and transport to the other components is illustrated in Figure 1-1.

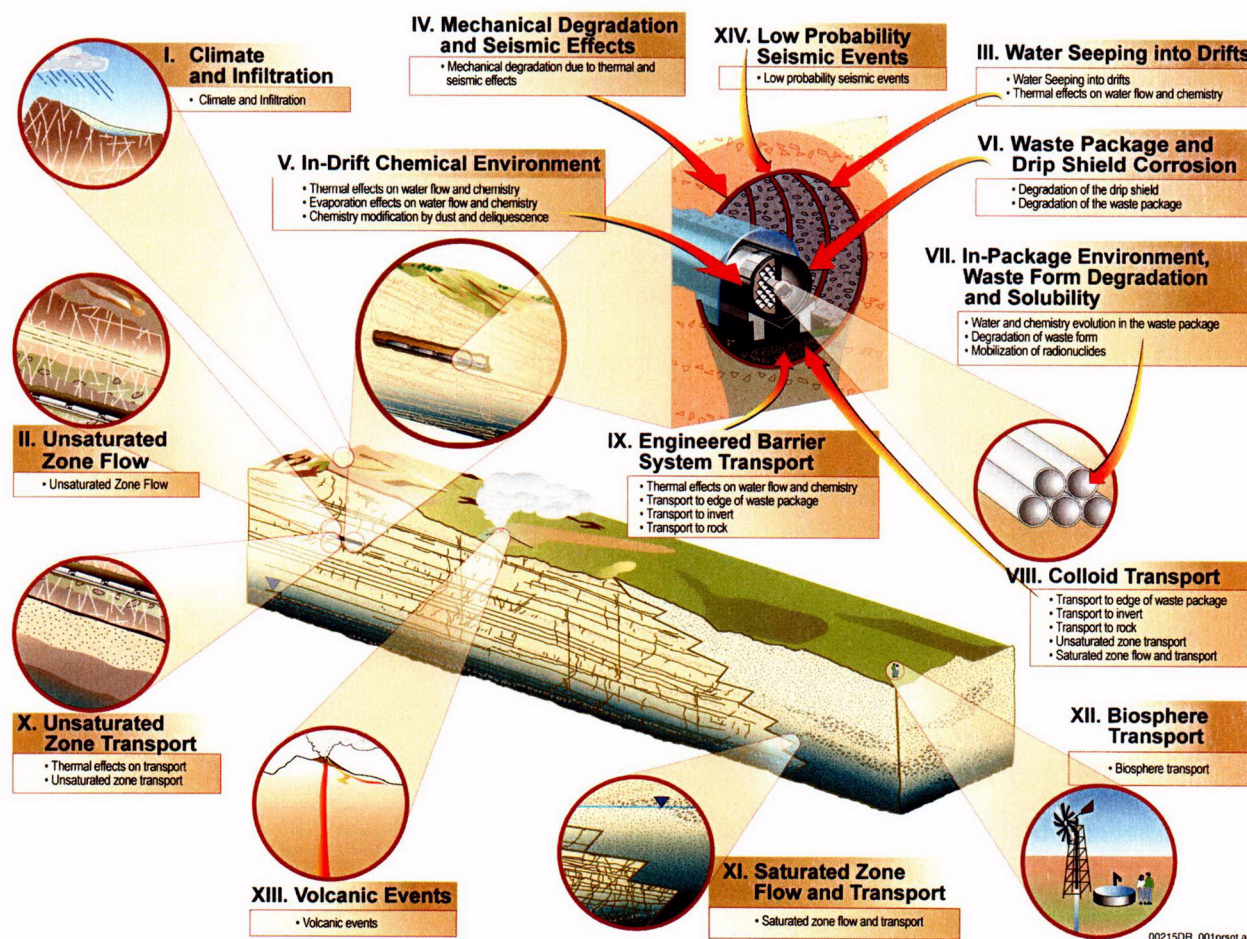


Figure 1-1. Components of the Postclosure Technical Basis for the License Application

Colloids and colloidal transport processes are treated as an integrated component of the postclosure technical basis because aspects of their behavior could impact the performance of the various engineered and natural features of the repository system. Therefore, although colloids are not a feature of the repository system in the same way as the waste package, unsaturated zone and saturated zone are, treating colloids as an integrated component assures proper consistency of their treatment across these features.

The information presented in this technical basis document, along with the associated references, provides a summary-level synthesis of the relevant aspects of colloid-facilitated radionuclide

transport and forms an outline of the ongoing development of the postclosure safety analysis that will be included in the license application (LA). This information is also used to respond to open Key Technical Issue (KTI) agreements made between the U.S. Nuclear Regulatory Commission (NRC) and the U.S. Department of Energy (DOE). Placing the DOE responses to individual KTI agreement and additional information needed requests within the context of the overall colloid transport processes, allows for a more direct discussion of the relevance of the agreement.

This technical basis document and appendices are responsive to agreements made between the DOE and the NRC during Technical Exchange and Management Meetings on Evolution of the Near-Field Environment (Reamer 2001a), Radionuclide Transport (Reamer and Williams 2000), and Total System Performance Assessment and Integration (Reamer 2001b). The appendices to this document are designed to allow for a transparent and direct response to each KTI agreement.

This technical basis document presents a summary and synthesis of the detailed technical information presented in the analyses and model reports and other technical products that are used as the basis for the description of the waste form, invert, unsaturated zone, and saturated zone features and the incorporation of those features into the postclosure performance assessment. Several analyses, model reports, and other technical products support this summary:

- *Site-Scale Saturated Zone Transport* (BSC 2003a)
- *Saturated Zone Colloid Transport* (BSC 2003b)
- *Saturated Zone Flow and Transport Model Abstraction* (BSC 2003c)
- *Saturated Zone In-Situ Testing* (BSC 2003d)
- *Site-Scale Saturated Zone Flow Model* (BSC 2003e)
- *EBS Radionuclide Transport Abstraction* (BSC 2001a)
- *Radionuclide Transport Models Under Ambient Conditions* (BSC 2001b)
- *Unsaturated Zone Flow Models and Submodels* (BSC 2001c)
- *Waste Form and In-Drift Colloids Associated Radionuclide Concentrations: Abstraction and Summary* (BSC 2003f)
- *Dissolved Concentration Limits of Radioactive Elements* (BSC 2003g)
- *In-Package Chemistry Abstraction* (BSC 2003h)
- *Particle Tracking Model and Abstraction of Transport Processes* (BSC 2003i)
- *In Situ Field Testing of Processes* (BSC 2001d)
- *Advection Versus Diffusion in the Invert* (BSC 2003j)
- *Engineered Barrier System: Physical and Chemical Environment Model* (BSC 2003k).

1.1 SUMMARY OF CONCEPTUAL UNDERSTANDING

Colloids are very fine particles ranging in size from 1 nm to 10 μm in characteristic dimension. Colloid transport may affect the rate of migration of contaminants in the subsurface environment relative to the transport of the contaminants as dissolved species. Potentially faster movement of colloids is the result of complex physical, chemical, electrical, and hydrodynamic phenomena acting on the colloids. These are phenomena that typically have not been associated with the transport of dissolved species. The potentially faster transport characteristic of colloids is generally referred to as the hydrodynamic chromatography effect (Haber and Brenner 1993).

Radioactive colloids (i.e., colloids that carry radionuclides) have been classified as either Type I colloids (either true or intrinsic) or Type II colloids (pseudocolloids). This classification was adopted to distinguish colloids resulting from nucleation or precipitation of dissolved radionuclides under chemically saturated conditions, which generate radionuclides in particulate form (true colloids), from colloids carrying radionuclides due to sorption of dissolved radionuclides onto natural or other colloids suspended in groundwater (pseudocolloids). This classification is used in this technical basis document.

There are several potential sources of colloids in groundwater, such as clay minerals, metal oxides, viruses, bacteria, and humic macromolecules (Chrysikopoulos and James 2003). It has been suggested (Haber and Brenner 1993) that dissolved groundwater contaminants could have a large affinity to sorption onto the surface of suspended colloids. As a result, colloids can possibly act as fast carriers for contaminants in subsurface environments and can be significant contributors to the rate of migration of contaminants, such as radionuclides potentially released from a repository system.

In order for colloids to provide a significant means for the transport of radionuclides from the waste form to the biosphere and, consequently, be a major contributor to dose, colloidal suspensions must: (1) contain high enough concentrations of colloids to carry a significant amount of radionuclides, either embedded in the colloids or attached on the surface of the colloids, relative to the concentration of dissolved radionuclides; (2) be stable for distances in the order of tens of kilometers and for time periods in the tens of thousands of years; and (3) not be appreciably filtered, reversibly or irreversibly, by the host rock. If one or more of these conditions are not met, colloids will not be significant to system performance of a high-level radioactive waste repository.

The main conclusion of this technical basis document is that colloid-facilitated radionuclide transport is not an important contributor to predicted system performance compared to transport of dissolved radionuclides. This conclusion is consistent with the opinions expressed by the International Review Team, which conducted a peer review of the total system performance assessment (TSPA) for the site recommendation. In its report, the International Review Team concluded that overly conservative assumptions may have been used in the modeling of colloid transport through the unsaturated zone (OECD and IAEA 2002, p. 39) and the saturated zone (OECD and IAEA 2002, p. 43). As a result of the conservatism used in the modeling of colloid transport of radionuclides, the International Review Team concluded that the importance of colloid transport's contribution to dose could have been "over rated."

1.2 PURPOSE

The purpose of this technical basis document is to present a screening of processes important to colloid-facilitated transport of radionuclides in the Yucca Mountain engineered and natural barrier subsystems that will demonstrate that the presence of colloids will not lead to the early and/or significant discharge of radionuclides to the biosphere, and hence, will not play a major role in the system performance.

Screening arguments will be presented for each of the subsystems, from the waste forms within the waste package to the boundary between the saturated zone and the biosphere. The technical basis supporting the process screening comprises the general theory of colloid stability, filtration, and radionuclide partitioning as documented in the scientific literature, and the results of Yucca Mountain Project (YMP) science activities that have studied the relevant physical/chemical processes for colloid generation in the waste package and transport of colloids from the waste package through the invert, unsaturated, and saturated zones.

1.3 SUMMARY CONCLUSIONS

To determine the importance of colloid-facilitated radionuclide transport to system performance, the pertinent processes regarding colloid transport in four repository subsystems are examined: waste package, invert, unsaturated zone and saturated zone. Some radionuclides (e.g., radionuclides of plutonium and americium) may be transported primarily in colloidal form during the 10,000-year regulatory period, while others are primarily transported as dissolved species (e.g., technetium, iodine, and neptunium).

As supported by the discussions in Sections 3, 4, 5, and 6 of this technical basis document, different processes impact the concentration of colloids in different repository subsystems. Within the drift environment, the key controlling factors are those that determine the stability of the colloidal suspensions. These factors are related to chemical conditions (such as high ionic strengths for the smectite colloids and a pH-ionic strength combination for the iron oxyhydroxide colloids) that cause the suspensions of both types of those colloids to be unstable during the first 2,000 to 3,000 years following waste emplacement. The instability of the colloid suspensions results in the colloids settling out. These same factors will also be the main contributors to the instability of colloid suspensions in the invert and the perturbed near field. Within the unsaturated zone and the saturated zone, filtration mechanisms will be the major contributors to reducing the concentration of colloids. Within the unsaturated zone, the interface between adjacent geologic units with sharply contrasting hydrologic properties will act as a barrier inhibiting colloids from moving through the downstream unit. Figure 1-2 shows qualitatively the impact of the different phenomena that lead to a decrease in the number of colloids in the repository subsystems, from the waste package to the biosphere.

The impact of the reducing concentration of colloids on radionuclide releases to the biosphere is shown qualitatively in Figure 1-3. Among all of the radionuclides, americium and plutonium are the ones of biggest concern with respect to colloidal transport because of their high affinity to attach to particle/solid surfaces. In Figure 1-3, the dissolved concentration of these two radionuclides is qualitatively compared to their concentration associated with colloids for the different repository subsystems, from the drift to the saturated zone. Because radionuclides that

adsorb to natural colloids may also adsorb to immobile material coated with secondary minerals, these radionuclides are eventually removed from the transporting fluid. The colloids of concern represent only a small fraction of waste degradation or rock alteration products. Figure 1-3 shows that the concentration of smectite colloids qualitatively drops significantly within the waste package until it reaches a constant value. This constant value qualitatively represents the natural concentration of smectite colloids available for reversibly sorbing radionuclides. The drop in the concentration of smectite colloids within the waste package is due to higher temperature and high ionic strength rendering the colloids unstable. Mills et al. (1991) concluded that metals strongly adsorbing onto natural colloids may also strongly adsorb onto the immobile matrix. It is thus anticipated that dissolved radionuclides, such as technetium and iodine, which are highly soluble, will be significantly more important to system performance than americium or plutonium, which are strongly associated with colloids. The screening arguments discussed in Sections 3, 4, 5, and 6 of this technical basis document support the conclusion that colloid-facilitated transport of radionuclides during the regulatory period is not as significant as transport of dissolved species for each of the four subsystems discussed. Consequently, colloid-facilitated radionuclide transport will not be significant to system performance.

The discussion in this technical basis document comprises a screening argument for processes governing colloid-facilitated transport of radionuclides at the Yucca Mountain repository. However, it is not suggested that colloid-facilitated transport be excluded from the TSPA. Rather, it is concluded that, on a risk basis, colloid-facilitated transport is not a significant contributor to system performance; therefore, uncertain technical issues associated with this transport mode are of relatively low importance compared to uncertain technical issues related to radionuclide transport as dissolved species. It is also concluded that, for purposes of the TSPA, the current treatment of colloid-facilitated transport of radionuclides is adequate.

1.4 ORGANIZATION OF TECHNICAL BASIS DOCUMENT

In addition to this introduction, this technical basis document consists of the following sections:

- Section 2—Colloid Stability, Filtration, and Radionuclide Partitioning: General Theory
- Section 3—Waste Package
- Section 4—Invert
- Section 5—Transport of Colloids in Unsaturated Zone
- Section 6—Colloid Transport in the Saturated Zone
- Section 7—Summary
- Section 8—References
- Appendix A—Exclusion of Entrained Colloids in Thermal-Chemical Alteration (Response to ENFE 1.06, ENFE 4.04 and GEN 1.01 (Comment #35))

- Appendix B—Sensitivity Analysis of Colloid Transport Parameters (Response to ENFE 4.06 AIN-1 and GEN 1.01 (Comments 35 and 37))
- Appendix C—Screening Out Coupled Thermal-Hydrologic-Chemical Effects (Response to ENFE 4.03 and GEN 1.01 (Comments 35 and 37))
- Appendix D—Contrasting Colloid Concentrations in the Engineered Barrier System and Saturated Zone (Response to TSPAI 3.30 and GEN 1.01 (Comments 43 and 46))
- Appendix E—Sensitivity Studies to Test Importance of Colloid Transport Parameters and Models (Response to RT 3.07 and GEN 1.01 (Comments 35, 43, and 46))
- Appendix F—Transport of Dissolved and Colloidal Radionuclides Through Invert (Response to TSPAI 3.17 and GEN 1.01 (Comments 36 and 38))
- Appendix G—Screening Criteria for Attachment of Radionuclides to Colloids (Response to RT 1.03 AIN-1, ENFE 3.05 AIN-1 and ENFE 4.05 AIN-1)
- Appendix H—Changes in Colloid Concentrations due to Shifts in pH and Ionic Strength (Response to TSPAI 3.42)

1.5 NOTE REGARDING THE STATUS OF SUPPORTING TECHNICAL INFORMATION

This document was prepared using the most current information available at the time of its development. This technical basis document and its appendices providing KTI agreement responses that were prepared using preliminary or draft information reflect the status of the Yucca Mountain Project's scientific and design basis at the time of submittal. In some cases, this involved the use of draft Analysis and Model Reports (AMRs) and other draft references whose contents may change with time. Information that evolves through subsequent revisions of the AMRs and other references will be reflected in the LA as the approved analyses of record at the time of LA submittal. Consequently, the Project will not routinely update either this technical basis document or its KTI agreement appendices to reflect changes in the supporting references prior to submittal of the LA.

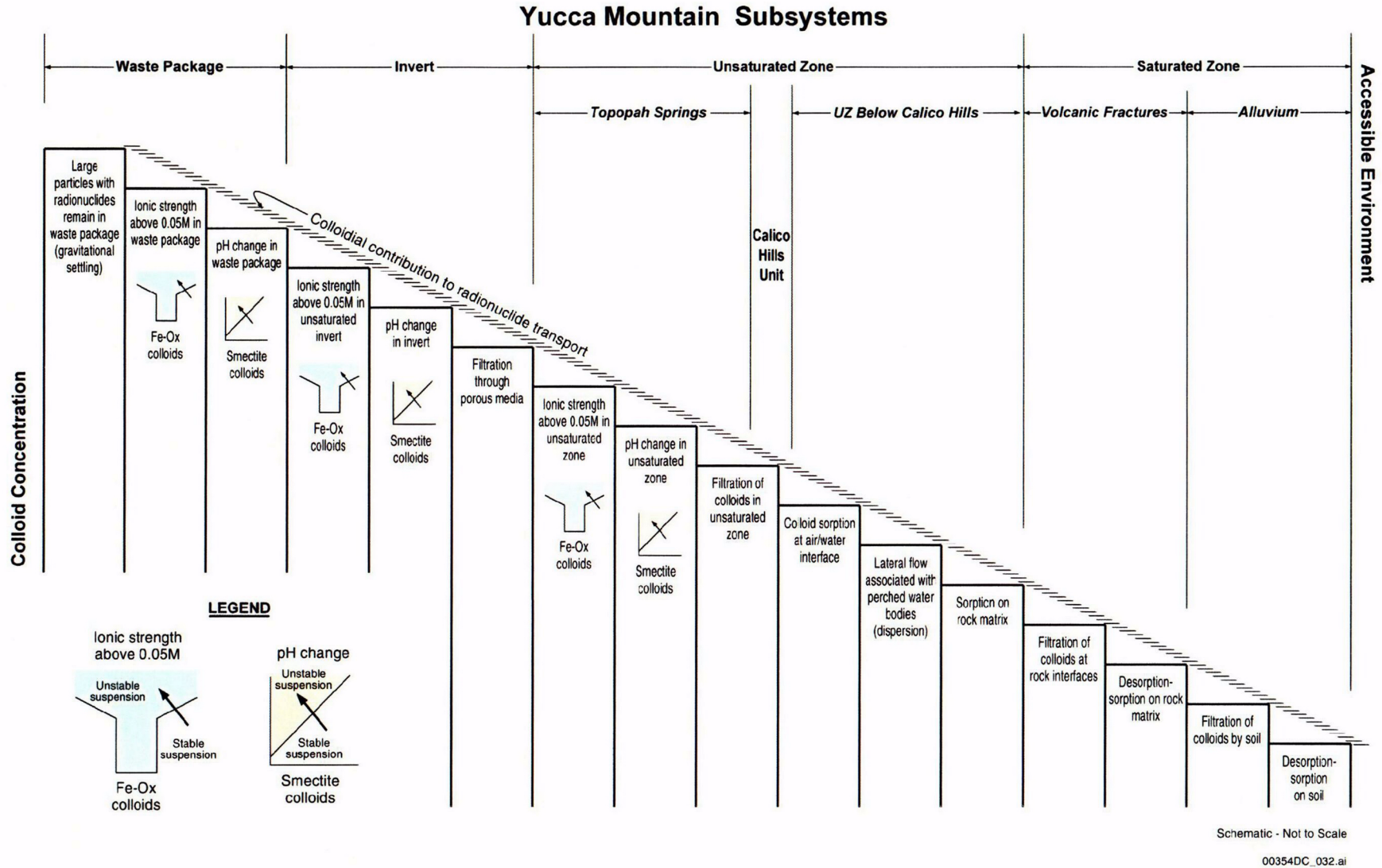
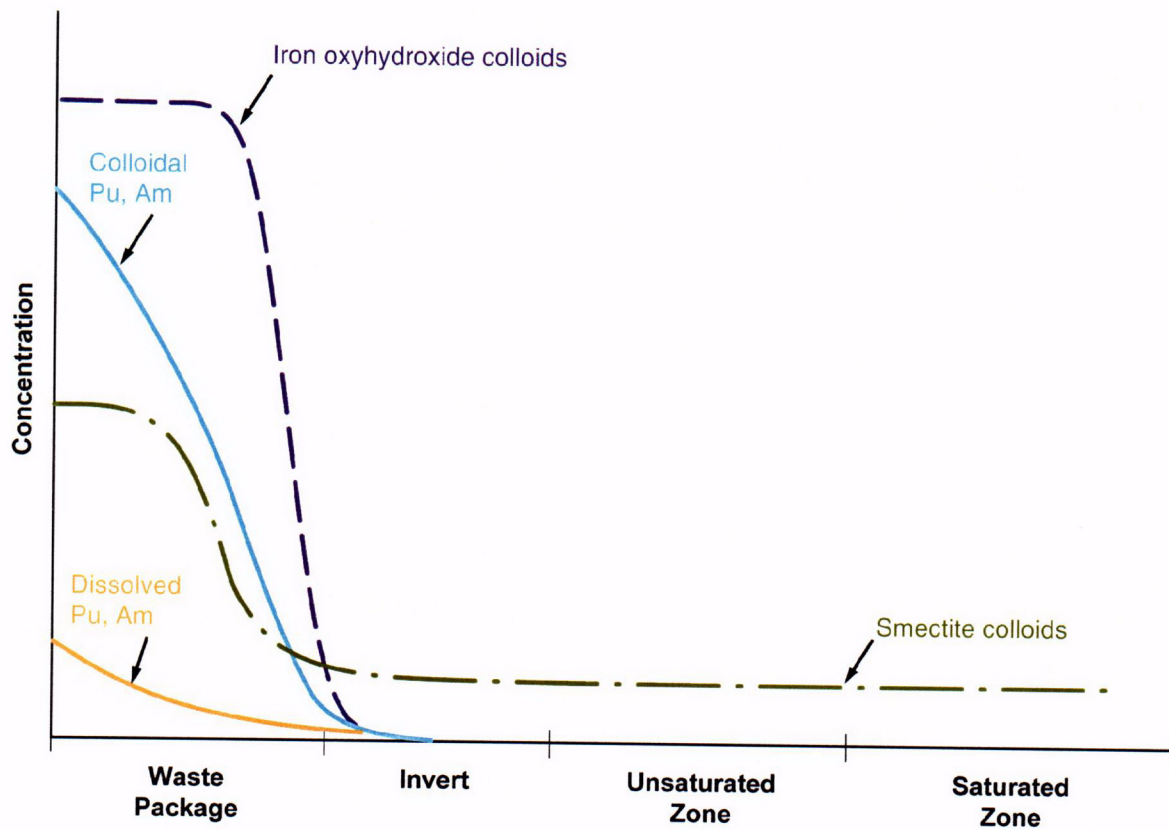


Figure 1-2. Processes Impacting Colloid Concentration from Drift to Biosphere Resulting in a Consistent Decrease in Colloid Concentration



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Figure 1-3. Schematic Representation of Radionuclide Concentrations (Plutonium and Americium) as Dissolved Species and Colloids from Drift to Biosphere

2. COLLOID STABILITY, FILTRATION, AND RADIONUCLIDE PARTITIONING: GENERAL THEORY

In this section, the general theory on the stability, transport and filtration, and sorption of radionuclides onto colloids is presented. A summary section is included presenting an overall picture of the potential impact of colloids on the performance of the repository system. This Section 2 is primarily based on a review of publications in the open literature. As appropriate, relevant information from YMP science activities is included to support the conclusions presented. It should be noted that the open literature, as well as that pertaining to repository systems has dealt mainly with colloid transport through saturated porous and fractured media.

2.1 STABILITY OF COLLOIDAL SUSPENSIONS

A key condition for colloid-facilitated transport of radionuclides to be a significant contributor to repository performance is the ability of the colloidal suspension to remain stable for distances of tens of kilometers and over tens of thousands of years.

The stability of colloidal suspensions against flocculation (also referred to as agglomeration or coagulation) of the colloids and deposition is governed by intercolloidal repulsive electrical forces, and these are a function of colloid number, density, size, composition, and surface chemistry (Haber and Brenner 1993), and attractive London-van der Waals forces that depend on the intercolloid separation distance and colloid size (Guzy et al. 1983; Elimelech and O'Melia 1990). In the 1940s and 1950s, the Derjaguin and Landau, and Verwey and Overbeek (Elimelech and O'Melia 1990) theory was used to explain colloid stability. The Derjaguin, Landau, Verwey and Overbeek theory defined the total interaction energy between colloids as a function of the separation distance between colloids. The total interaction energy is the sum of the energy of the electric double layer and the London-van der Waals energy. In addition, physical effects, such as flow rate and gravitational forces, and chemical conditions (the latter determining the colloid surface charge) also influence the intercolloid interactions that could lead to flocculation and gravitational settling of the particles (Guzy et al. 1983; Elimelech and O'Melia 1990).

While gravitational settling is directly proportional to the third power of particle size, larger colloids tend to form more stable suspensions in natural systems due to size-exclusion effects (Haber and Brenner 1993). However, this should not be interpreted to mean that colloids, particularly in the higher end of the size spectrum (i.e., about 10 μm in diameter), will be stable over the temporal and spatial scales of relevance to repository performance. Several researchers have concluded that it is difficult to envision colloidal suspensions remaining stable, and therefore mobile, for large distances and long times (Mills et al. 1991; van der Lee et al. 1994). Elimelech and O'Melia (1990) have concluded that even for very stable colloidal suspensions, the attachment of the colloids to the wall of the flow channel may be significant.

The interaction between colloids is governed by the sum of the electric repulsion force due to identical surface charges (known as the electric double-layer force) and the attractive London-van der Waals force (Elimelech and O'Melia 1990). The electric double-layer force stems from approaching colloids having equal surface charges. Each colloid is surrounded by a layer of oppositely charged ions that counterbalances the colloid surface charge. The

London-van der Waals attractive force is a function of distance between approaching colloids and the colloids' size. It has been shown that the strength of the London-van der Waals force is inversely proportional to the distance between the colloids and the colloid size (Guzy et al. 1983). That is, the closer the colloids are to each other and the smaller they are, the higher the strength of the attractive force.

There are several factors that affect the strength of the repulsive electric double-layer force; the zeta potential (a measure of the surface charge), colloid size, and ionic strength and temperature. Ionic strength and temperature have a considerable impact on the thickness of the electrical double layer (Guzy et al. 1983). The double-layer thickness is inversely proportional to the square root of temperature and to the square root of the ionic strength (Guzy et al. 1983, Equations 47 and 48). Thus, higher ionic strengths and higher temperatures lead to thinner electric double layers and hence weaker repulsive forces between colloids. As temperature and ionic strengths increase, the repulsive force decreases allowing the attractive London-van der Waals forces to dominate colloidal particle interactions.

These results are consistent with others reported in the literature. For example, Langmuir (1997, p. 439) states that a colloidal suspension's stability ratio is inversely proportional to temperature. In *Waste Form and In-Drift Colloids Associated Radionuclide Concentrations: Abstraction and Summary* (BSC 2003f), experimental results demonstrate that colloid suspensions become more unstable with increasing ionic strength.

As discussed in Section 3, during the first one-third of the 10,000-year postclosure regulatory period, the high temperature will result in water evaporation and increased ionic strengths rendering colloids important to radionuclide transport unstable. This will decrease the concentration of colloids either carrying or able to carry radionuclides for the waste package. Even after 10,000 years, the temperature within the emplacement drifts is expected to be 20° to 25°C higher than the host-rock ambient temperature (BSC 2003l, Figure 6.5.2-1).

2.2 COLLOID FILTRATION

As colloids travel along the flow path from the repository to the biosphere, they will undergo interactions with the host rock. Larger colloids are likely to be physically trapped within the pores in the rock matrix. If colloids are bigger than the pore size through which they are attempting to pass, the particles will not be able to get past the pore entrance. Smaller colloids that can enter the pore are likely to come in very close proximity with each other to overcome any possible repulsive forces between the colloids and flocculate, thus, forming larger particles that will then get trapped within the pores. The smaller colloids (i.e., diameter less than 1 μm) will be subjected to Brownian deposition onto the rock matrix (Haber and Brenner 1993), thus, reducing the number of colloids entrained in the flow.

Colloid filtration is also called colloid attachment or colloid deposition. There are many different studies regarding the transport of and deposition of colloidal particles through fractures under saturated flow conditions; some examples are Haber and Brenner (1993), van der Lee et al. (1994), Chrysikopoulos and James (2003), Chrysikopoulos and Abdel-Salam (1997), and James and Chrysikopoulos (1999, 2000, 2003). There have been other studies aimed at understanding the kinetics of colloid interactions leading to deposition on the surfaces of immobile phases in

porous media. Some examples are Guzy et al. (1983), Elimelech and O'Melia (1990), and Adamczyk et al. (1992a, 1992b). Even though the latter works were for porous media, the kinetic models apply equally to the interactions between colloids and fracture surfaces because (1) the ratio of the characteristic dimension of the colloids to the characteristic dimension of the immobile phase was considered to be much smaller than one, and (2) the interactions between colloids and the immobile phases are only important at separation distances much smaller than the colloid characteristic dimension. Consequently, as the colloids approach the immobile phase, the immobile phase looks and behaves like a planar surface from the perspective of the colloids.

As colloids move down a fracture, they will be affected by (1) hydrodynamic and physical forces in the directions parallel to the fracture walls and (2) external physical, chemical, and electrical forces in the direction normal to the fracture walls. Hydrodynamic forces account for the drag that the flow exerts on the colloids leading to entrainment of the colloids in the flow and gravitational effects. External forces include gravitational effect, London-van der Waals attractive force, and electric double-layer force. In addition, the external forces account for lubrication effects that colloids are subjected to as they approach the immobile phase.

Finally, colloids are subjected to Brownian motion, which is typically modeled using an equivalent diffusivity. The Brownian diffusivity is directly proportional to temperature and inversely proportional to colloid size (Guzy et al. 1983). The effects of Brownian motion are more pronounced for colloids of less than 1 μm in characteristic dimension.

The theoretical studies regarding colloid transport through porous and fractured media are generally consistent regarding the effect of colloid size on transport times. Larger colloids are transported at a faster rate than smaller ones, with the latter showing a larger propensity to deposit onto the immobile rock. Comparisons of experimental and theoretical results for colloid deposition reported by Elimelech and O'Melia (1990) show increased deposition rates measured experimentally than predicted theoretically. Those experimental results also suggest that in natural waters colloid deposition is independent of size. Elimelech and O'Melia (1990) attribute this discrepancy to failure of the Derjaguin, Landau, Verwey and Overbeek theory to account for the dynamic interactions between colloids and the immobile phase.

Colloid filtration will be an important phenomenon resulting in the decrease of the colloid concentration, particularly within the unsaturated zone directly below the repository.

2.3 RADIONUCLIDE PARTITIONING BETWEEN COLLOIDS AND DISSOLVED SPECIES

Radionuclides can potentially be transported from the waste form to the biosphere as either dissolved species or in colloidal form. In order for colloid transport to be a significant contributor to the discharge of radionuclides to the biosphere, colloids must carry a significant mass of radionuclides.

As discussed in Section 3, the most likely forms of radioactive colloids under the expected conditions at the Yucca Mountain repository are: (1) colloids with embedded radionuclides resulting from the degradation of defense high-level radioactive waste glass, referred to as "waste-form colloids"; (2) colloids formed as a result of corrosion of steel components within the

repository, referred to as “iron oxyhydroxide colloids”; and (3) natural groundwater colloids, referred to as “smectite colloids.” The formation of colloids due to hydrolysis or polymerization of dissolved actinides (referred to as “true” or “intrinsic colloids”) is not considered because recent experiments have demonstrated that these colloids dissolve under the expected repository conditions (see Section 3 of this technical basis report). First, in the tests performed at Argonne National Laboratory for degradation of defense high-level radioactive waste glass (Ebert 1995, Sections 6.2.1 and 6.2.2), no evidence was found of the formation of true colloids. Second, degradation of commercial spent nuclear fuel (CSNF) may form true colloids close to the fuel surface where the fluid may be saturated with respect to uranium, but these true colloids are likely to dissolve in unsaturated fluid.

Besides the mass of radionuclides that can be embedded in waste-form colloids from the degradation of defense high-level radioactive waste glass, dissolved radionuclides can be adsorbed onto the surface of colloids to form “pseudocolloids.” Only plutonium and americium are expected to be embedded in colloids resulting from the degradation of defense high-level radioactive waste glass. Thus, the discussion herein focuses on the sorption of dissolved radionuclides onto the surface of available colloids.

A key consideration in the assessment of colloid contribution to radionuclide transport is determining the partition coefficients between interstitial solvent (i.e., dissolved in the groundwater), the immobile phase of the host rock (i.e., sorption within the porous rock and the fracture surfaces), and the surfaces of the mobile colloids (Haber and Brenner 1993).

Transport of groundwater colloids is likely to be preferentially through fractures in the unsaturated zone (see Section 5) and in the fractured volcanics within the saturated zone (Section 6). The stability of a colloidal suspension increases with particle size because of the reduced number of particles per unit volume that can collide (i.e., the larger the colloids the more stable the suspension will be and the higher the probability that the colloids will remain entrained in the groundwater flow) (Haber and Brenner 1993). However, larger colloids are unlikely to be effectively transported through the unsaturated zone and the volcanic fractures in the saturated zone in the vicinity of Yucca Mountain due to simple geometric considerations (BSC 2003m, Section 6.18). Larger colloids are more likely to be physically trapped in the pore constrictions and do not penetrate the porous matrix. As noted in *Radionuclide Transport Models Under Ambient Conditions* (BSC 2003m), colloids are discharged to the unsaturated zone directly into fractures for the model elements corresponding to the repository.

During transport through fractures as both dissolved species and in colloidal form, radionuclides undergo (1) sorption of dissolved radionuclides onto the fracture surfaces, (2) sorption of dissolved radionuclides onto the porous matrix following diffusion, (3) sorption of dissolved radionuclides onto the surface of colloids, (4) attachment of radioactive colloids onto the surface of fractures (filtration), (5) transport as dissolved species and as colloids, (6) diffusion of dissolved radionuclides from the fractures into the porous matrix, and (7) decay. The conservation equation for each radionuclide needs to account for all of these phenomena to adequately estimate the amount of radioactive species discharged to the biosphere. Diffusion of the larger, more stable colloids into the rock matrix is not considered an important phenomenon because of the very low probability of the larger colloids being able to physically penetrate into the pores (BSC 2003m, Section 6.18).

Sorption of dissolved radionuclides onto the fracture surfaces and onto the rock matrix after diffusion has been traditionally treated using an equilibrium isotherm model and defined by a distribution coefficient. Diffusion of dissolved species from the fractures into the rock matrix has been treated using a flux boundary condition at the fracture–matrix interface based on Fick’s law of diffusion. These modeling approaches are well established and accepted (de Marsily 1986).

Sorption of radionuclides onto the surface of colloids depends on a number of phenomena; namely: (1) electrostatic forces, (2) ion exchange, (3) surface reactions, and (4) co-precipitation (BSC 2003f). These are complex phenomena, and it has been assumed that the effect of these phenomena can be captured using the linear isotherm model for reversible sorption (BSC 2003f). However, for this assumption to be applicable, some important conditions must exist. First, the dissolved radionuclide–colloid system must be in thermodynamic equilibrium. Second, the rate of radionuclide sorption must be linearly correlated to the concentration of dissolved radionuclides. Third, the rate of sorption must be independent of other solutes present in the groundwater. Fourth, the entire colloid surface area must be available for sorption. The likelihood that these conditions are met under repository conditions is not particularly high (BSC 2003f).

Haber and Brenner (1993) investigated the sorption of dissolved contaminants onto the surface of colloidal particles under both equilibrium and nonequilibrium conditions. They developed a mathematical expression for the rate of solute sorption from the solvent onto the surface of colloids for nonequilibrium conditions (Haber and Brenner 1993, Equation 2.9b). That expression demonstrates that, under nonequilibrium conditions, the rate of sorption increases linearly with the solute concentration and decreases linearly with the concentration of solute already adsorbed onto the surface of colloids. The key parameter in the Haber and Brenner expression for nonequilibrium sorption is a mass transfer coefficient. The asymptotic limit of the Haber and Brenner expression for high values of the mass transfer coefficient is the linear isotherm model.

The Haber and Brenner nonequilibrium sorption expression indicates that under nonequilibrium conditions the use of the linear isotherm model to describe the sorption of solutes onto the surface of colloids will overestimate the mass of solutes adsorbed.

In *Waste Form and In-Drift Colloids Associated Radionuclide Concentrations: Abstraction and Summary* (BSC 2003f) it was concluded that equilibrium conditions are not expected at the Yucca Mountain repository. This conclusion, combined with the work of Haber and Brenner (1993), shows that the mass of radionuclides that can be transported as pseudocolloids will be overestimated by using a linear isotherm model to describe the partitioning of radionuclides between dissolved species and colloids.

The mass of dissolved radionuclides that can be adsorbed onto the surface of colloids is a function of the colloids’ surface area per unit volume (BSC 2003f). Larger colloids, the ones that could transport farther in the fractures, have a smaller surface-area-to-volume ratio than the smaller colloids. The smaller colloids are more susceptible to attachment to the fracture walls.

The mass of radionuclides that can adsorb onto colloids will also be a function of the colloid concentration. The higher the concentration of colloids, the higher the colloidal surface area available to compete with the immobile rock surfaces for sorption of radionuclides. Analyses of colloid concentrations and size distributions in Yucca Mountain groundwaters have found colloid concentrations to be too low for significant colloid-facilitated transport of radionuclides (DOE 2002, pp. 4-335 to 4-336). Moreover, Triay et al. (1996), in a compendium of colloid concentration as a function of water chemistry, found that under thermal and chemical conditions similar to those expected at Yucca Mountain, colloid concentrations are unlikely to be high enough for colloids to effectively compete with the immobile rock for the sorption of dissolved radionuclides, particularly when the immobile rock is coated with secondary minerals.

As dissolved radionuclides travel from the repository towards the biosphere, their concentration is expected to decrease due to the various retardation processes that the radionuclides undergo, such as diffusion on the rock matrix and sorption onto the surfaces of the fractures and within the rock matrix. These processes act as effective mass sinks for dissolved radionuclides. This means that there will be lesser amounts of dissolved radionuclides available for sorption onto colloids and a lower likelihood for the formation of radioactive colloids. It is possible that far away from the repository desorption of radionuclides from the surface of colloids will take place, as discussed in the following paragraph. Based on conclusions reached by Mills et al. (1991), van der Lee et al. (1994) questioned whether colloid-facilitated transport of radionuclides would be significant at a nuclear waste disposal site.

Mills et al. (1991) evaluated the transport of colloids and metals in porous media. They analyzed the transport of only dissolved species (solutes) under a variety of transport conditions and repeated the analyses under the same conditions including colloids. The basic system Mills et al. (1991) analyzed consisted of a contaminant source located in an unsaturated zone and the transport of the contaminants to a receptor downgradient in a saturated zone. The solute-colloid transport analyses considered uncertainty in several key parameters: source duration (1,000 and 100,000 years), natural colloid concentration (0, 10, and 100 mg/l), infiltration rate (0.007 and 0.35 m/year), partition coefficient for adsorption of solutes onto colloids (10^3 , 10^4 , and 10^5 l/kg) and partition coefficient for adsorption of solutes to the immobile soil matrix (0, 10, 10^2 , 10^3 , 10^4 , and 10^5 l/kg). Mills et al. (1991, p. 206) concluded that, "As colloids move through subsurface media, and if adsorbed metal species are present, then the colloids reach a 'clean' portion of the aquifer, solutes are rapidly adsorbed to the aquifer-soil matrix and rapidly desorbed from the colloids to reestablish a new equilibrium between solute and colloid-adsorbed species. Thus, the colloids are rapidly stripped of adsorbed metal species and continue migrating with relatively little metal adsorbed." According to Mills et al. (1991), this desorption phenomenon explains their results in which, for many of the cases they analyzed, the impact of colloid transport on the total mobile phase concentration (dissolved metal concentration plus metal concentration adsorbed to mobile colloids), in terms of either increased concentration or early arrival at the receptor location, was not "remarkable." Mills et al. (1991, p. 206) further concluded that, "Typically, when travel times to a source are thousands of years in the absence of colloids, the travel times still remain on the order of thousands of years in the presence of colloids."

2.4 SUMMARY AND CONCLUSIONS

While the potential exists for fast transport and early release of radioactive colloids to the biosphere at the Yucca Mountain repository, several conditions must simultaneously be met for transport of radioactive colloids to be a significant contributor to dose. Those conditions are:

- Colloids must be present in high enough concentrations and provide high surface area per unit volume to carry a significant amount of radionuclides, either embedded in the colloids or attached on the surface of the colloids, relative to the concentration of dissolved radionuclides.
- Colloidal suspensions must be stable for distances in the order of tens of kilometers and for time periods in the tens of thousands of years.
- Radioactive colloids must not be appreciably filtered, reversibly or irreversibly, by the host rock.

If any one of these conditions is not met, the likelihood that colloid transport provides a significant transport mechanism for the release of radionuclides to the biosphere is low.

The higher temperatures and higher ionic strength within and in the vicinity of the repository during the first one-third of the postclosure regulatory period are expected to result in unstable colloidal suspensions.

As radionuclides adsorb onto the surface of colloids, they may neutralize negative colloid surface charges, thus rendering the colloids more susceptible to filtration by attachment to the surface of fractures, particularly if the fractures are coated with secondary minerals. Therefore, radionuclide sorption may have a beneficial effect on decreasing the potential for fast transport of radioactive colloids.

As radionuclides move farther away from the repository, their concentration as dissolved species decreases; therefore, there will be less mass of dissolved radionuclides available for sorption onto colloids. Diffusion into and sorption onto the rock matrix lead to the decrease in the concentration of dissolved radionuclides. It has been concluded (Mills et al. 1991) that over long distances and long travel times, a decrease in dissolved contaminants concentration far away from the source can result in desorption of contaminants from the surface of colloids. This potential desorption process has led some researchers to conclude that when contaminant travel times are thousands of years in the absence of colloids, they are also thousands of years in the presence of colloids.

Most contaminant transport studies reported in the literature pertain to saturated conditions. There is little information regarding the transport of colloids under unsaturated conditions. This seeming lack of information for unsaturated systems notwithstanding, some intuitive arguments based on physics can be made regarding colloid transport in unsaturated conditions. Assuming that the flow in the unsaturated zone below the proposed repository horizon is primarily films of groundwater adjacent to the fracture walls, then only colloids of a size considerably smaller than the films could be transported with the groundwater flow. Also, as stated earlier, the smaller

colloids are more susceptible to Brownian deposition and, hence, to attachment to the fracture walls. Finally, the colloids within the groundwater film could be physically closer to the fracture walls to enhance attachment to the latter by other mechanisms.

3. WASTE PACKAGE

This section of the technical basis document summarizes the current understanding of the formation of radionuclide-laden colloids, prediction of their concentration within the waste package and their release into the invert. The waste package is the first of the repository system subfeatures examined to determine the importance of colloid-facilitated radionuclide transport with respect to the postclosure performance of the Yucca Mountain repository, as shown in Figure 1-1. This section provides a summary-level synthesis of the processes and phenomena governing the formation, prediction of their concentration, and transport of radionuclide-carrying colloids within the waste package. The modeling assumptions to be used in the TSPA for the LA (TSPA-LA) are discussed. In preparing this section, information has been summarized from the following pertinent analysis and model reports, as well as other technical products:

- *Multiscale Thermohydrologic Model* (BSC 2003n)
- *Engineered Barrier System: Physical and Chemical Environment Model* (BSC 2003k)
- *In-Package Chemistry Abstraction* (BSC 2003h)
- *Dissolved Concentration Limits of Radioactive Elements* (BSC 2003g)
- *Waste Form and In-Drift Colloids Associated Radionuclide Concentrations: Abstraction and Summary* (BSC 2003f).

3.1 DESCRIPTION OF RELEVANT PROCESSES AROUND WASTE PACKAGE

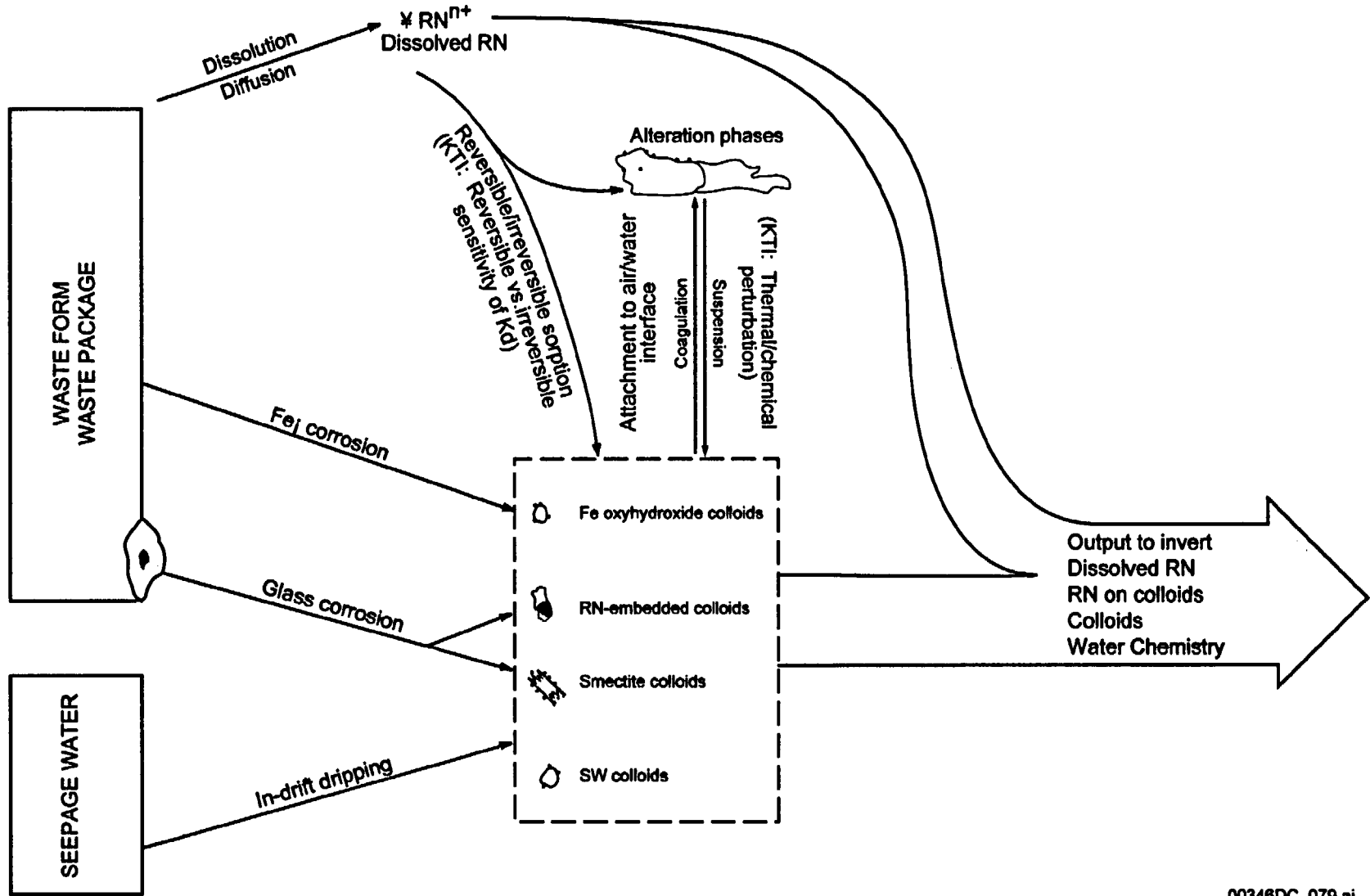
The relevant physical/chemical processes for colloid generation and transport inside waste packages prior to any disruption by igneous intrusion are shown in Figure 3-1.

3.1.1 In-Drift and In-Package Chemistry

The evolution of general physical and chemical environments is important for understanding colloid generations and stabilities inside the drift and the waste package. Detailed analyses of in-drift thermal-hydrologic conditions are documented in the *Multiscale Thermohydrologic Model* (BSC 2003n, Figure 6.3-12). A typical evolution of temperature, relative humidity, and liquid-phase saturation degree over time is illustrated in Figure 3-2. Relative humidity decreases to low values shortly after emplacement of the waste packages. As the waste packages cool over time, relative humidity begins to rise until it reaches 100 percent after a few thousand years. During the period with relative humidity less than 98 percent, any dilute species in groundwater flowing into the drift become concentrated by evaporation, which results in a high ionic strength solution, which, in turn, destabilizes colloid suspensions. The ionic strength of some representative seepage waters as a function of relative humidity is shown in Figure 3-3 (BSC 2003k). As long as the relative humidity is less than 98 percent, the representative solutions have an ionic strength greater than the upper limit of colloid stability (0.05 M) (BSC 2003f, Sections 6.3.2.2 and 6.3.2.3). Therefore, the formation of a stable colloid suspension during the first thousand years after closure is unlikely. Colloid transport can be possible only after the effects of evaporation cease to be significant after the thermal period when temperatures are below 90°C (Figure 3-2).

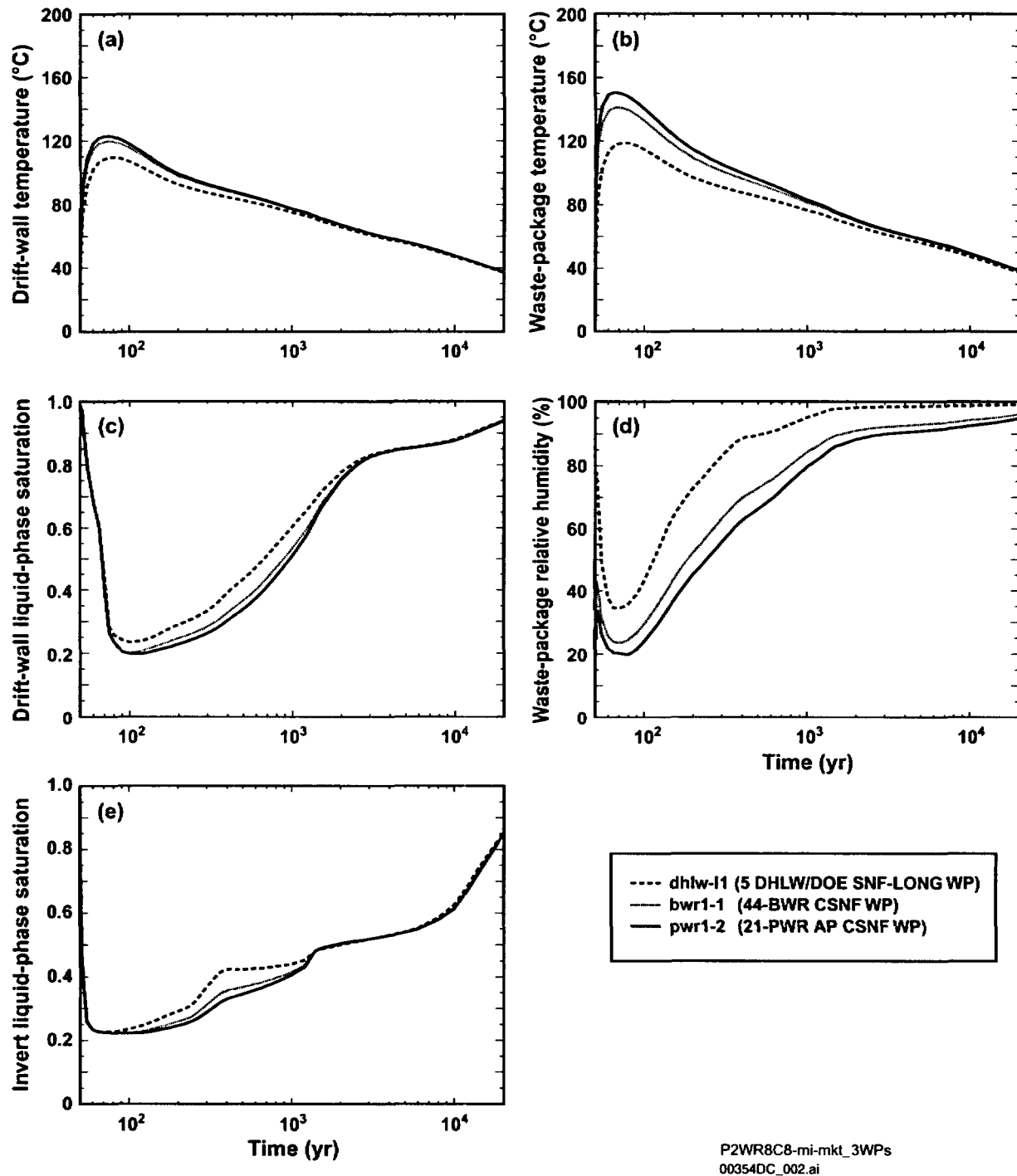
Furthermore, the degradation of the waste form and the waste package can lead to the formation of concentrated solutions. In process modeling, in-package chemistry has been predicted for two scenarios—water vapor condensation and seepage water dripping—with an assumption of no water evaporation. For the scenario of seepage water, the reaction-path calculations show that the initial seepage-water compositions are quickly modified by water-package chemistry produced as components within the waste package degrade (BSC 2003h). Depending on the conditions, in most cases, the resulting solution can attain ionic strength higher than 0.05 M as the water-waste package reaction progresses (Figure 3-4). Under such conditions, a stable colloid suspension, if there is any, will become unstable. This prediction is consistent with the observation in the static-saturated tests that colloid concentrations increase with time, up to the point where the colloid concentrations reach maximum values and start to decrease (Figure 3-5).

In summary, the formation of a stable colloid suspension during the first few thousand years of the regulatory period is unlikely because of evaporation during the thermal period. Colloids could be generated at a late stage of the regulatory period, when evaporation becomes less effective. However, these colloids can be destabilized by high ionic strength environments that can be potentially created during waste degradation. Therefore, the general physical/chemical environments have imposed restrictive constraints on colloid stability inside the drift. It is expected that in-drift colloid transport can be possible only for limited time periods and limited combinations of physical and chemical conditions.



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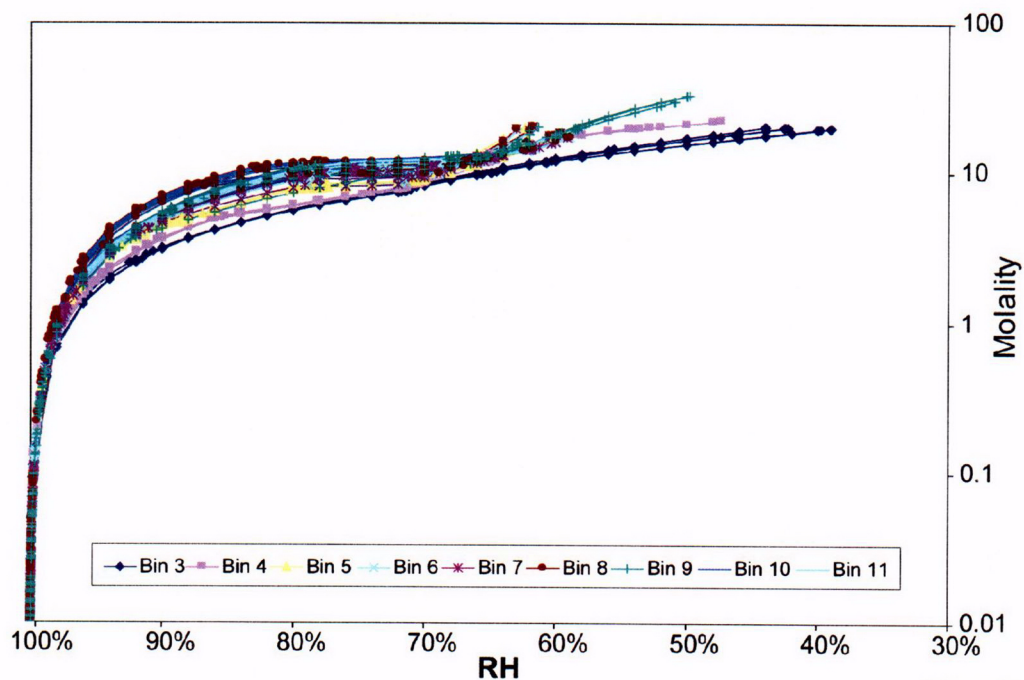
Figure 3-1. Relevant Physical and Chemical Processes for Colloidal Generation and Transport from Waste Forms and Waste Packages



Source: BSC 2003n, Figure 6.3-12.

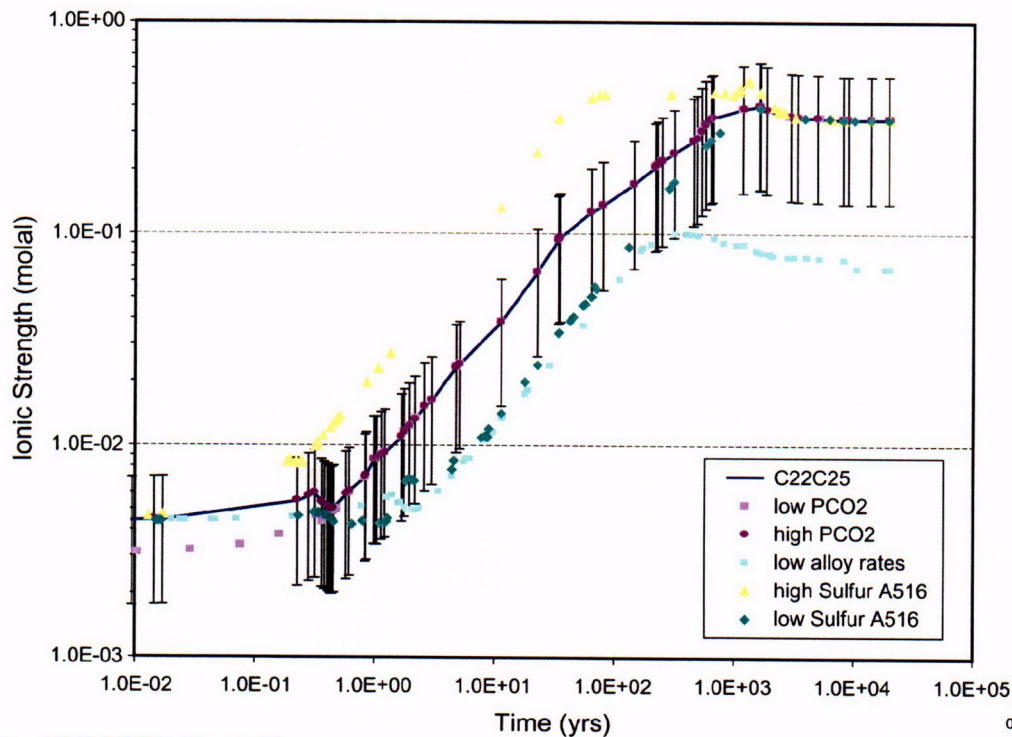
NOTE: These waste packages bracket the entire range of temperature at this location.

Figure 3-2. Thermal-Hydrologic Conditions for the Mean Infiltration-Flux Case for a Range of Waste Packages at the P2WR8C8 Location in the Tptpmn (tsw34) Unit



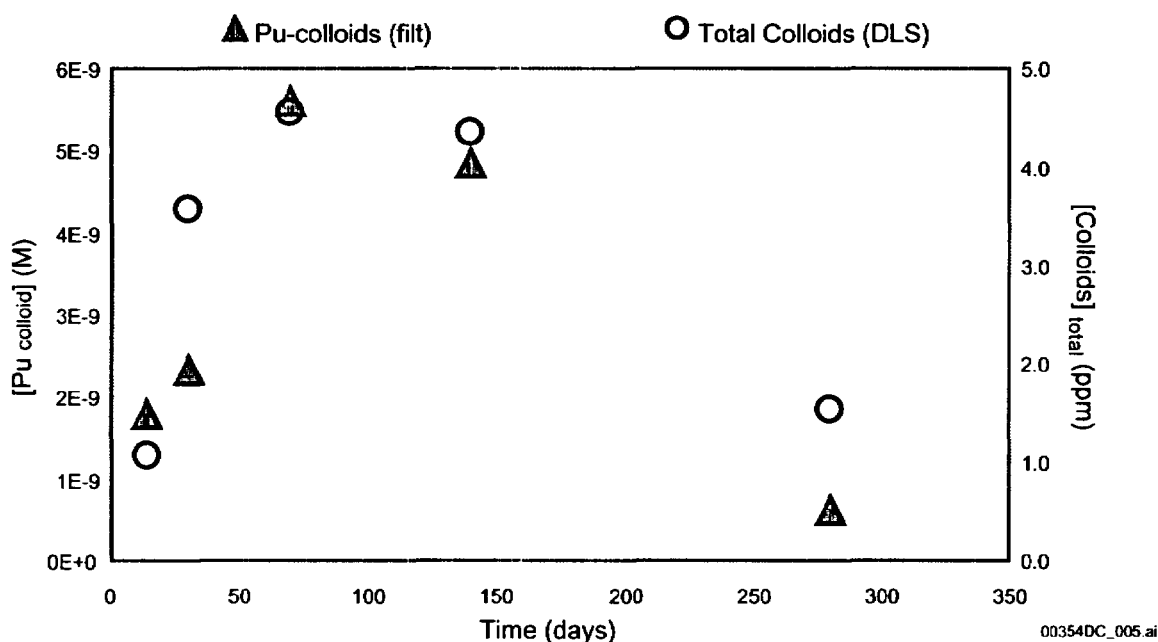
Source: BSC 2003k, DTN: MO0308SPAPCESA.001.

Figure 3-3. Ionic Strength (in Molality) of Some Representative Seepage Waters as a Function of Relative Humidity



Source: BSC 2003h, Figure 11.

Figure 3-4. An Example of Ionic Strength Evolution during the Degradation of Commercial Spent Nuclear Fuels under the Assumption of No Water Evaporation



Source: BSC 2003f, Figure 3. DTN: LL991109751021.094.

Figure 3-5. Concentrations of Plutonium and Colloids as a Function of Defense High-Level Radioactive Waste Glass Corrosion Test Duration

3.1.2 Waste Types and Potential Colloid Types

As explained later in Section 3.4, three types of colloids are modeled in the current waste package model abstraction:

- Natural colloids in seepage water/groundwater include mineral fragments, humic substances, and microbes. Humic substances are not sufficiently abundant in Yucca Mountain groundwater to impact transport (Minai et al. 1992). Microbes are susceptible to filtration due to their large sizes (~1 to 10 μm). (See Section 3.2.6.). The mineral colloids are represented as smectite colloids (BSC 2003f).
- Corrosion product colloids are derived from the corrosion of waste package and metallic inert materials. These colloids are primarily composed of iron oxyhydroxides. The concentration range of the colloids is estimated based on experiments performed at the University of Nevada, Las Vegas on scaled-down miniature waste packages (DTN: MO0212UCC034JC.002; BSC 2003f).
- Waste form colloids are formed from the corrosion of defense high-level radioactive waste glass. Glass waste forms tested include Savannah River Laboratory and West Valley Demonstration Project glasses (CRWMS M&O 2001a; BSC 2003f). (Glass is not available from the yet-to-be-built Hanford vitrification plant.) Colloids produced from both waste forms are primarily smectite clays containing measurable plutonium, as well as discrete radionuclide-bearing phases including brockite (thorium-calcium orthophosphate) and an amorphous thorium-titanium-iron silicate, similar to thoriutite.

Long-term corrosion testing of CSNF and DOE spent nuclear fuel (DSNF) under hydrologically unsaturated, oxidizing conditions has been conducted. Results from this testing show both very low colloid concentrations and low fractions of uranium in the colloid mass (Mertz et al. 2003). Thus, colloids from both CSNF and DSNF are excluded in the colloidal modeling. Note that CSNF accounts for the major fraction of the wastes by metric tons of heavy metal to be emplaced in the Yucca Mountain repository.

The formation of true or intrinsic colloids depends on the degree of saturation of the solution (i.e., the solution must be supersaturated) with respect to the corresponding radionuclide-bearing mineral phase. There has been no evidence of their formation in the tests performed at Argonne National Laboratory for degradation of defense high-level radioactive waste glass. Degradation of CSNF may form true or intrinsic colloids (e.g., schoepite), but they are likely to dissolve in groundwater in the unsaturated zone. In the Argonne National Laboratory tests (Mertz et al. 2003), it was observed that these metastable colloids dissolved upon the introduction of J-13 groundwater. J-13 groundwater was assumed to be a lower bound with respect to the temperature and chemistry of water inside the drift. Typical water inside the drift is expected to be at a higher temperature and have higher ionic strength than J-13 water. Consequently, colloids will dissolve more readily in the water inside the drift than in J-13 groundwater. Therefore, the possibility of formation of intrinsic colloids is eliminated from further consideration in the colloid modeling (BSC 2003f, Section 6.3.1).

3.1.3 Radionuclide Sorption onto Colloids

The effectiveness of colloid-facilitated transport depends on the sorption capability of colloids for radionuclides of interest. For reversible sorption processes, a linear isotherm model is used:

$$m_c = K_d m_d \quad (\text{Eq. 3-1})$$

where m_c is mass of radionuclide adsorbed on a unit of mass of solid; m_d is the concentration of dissolved radionuclide; and K_d is the distribution coefficient. The ranges of K_d values are derived from literature data, which are obtained mostly from noncolloidal systems.

The results of experiments with plutonium and americium with colloidal hematite and goethite show that the rates of desorption of these radionuclides are significantly lower than the rates of sorption. Over a time period up to 150 days, the extent of desorption is considerably less than that of sorption. Based on these data (Lu et al. 1998) and observations from field studies (Brady et al. 2002), 90 to 99 percent of sorbed plutonium and americium onto iron oxyhydroxides are modeled as irreversibly adsorbed (BSC 2003f).

Colloid Filtration—Colloids generated within the defense high-level radioactive waste glass and at its outer surfaces can be filtered. Removal of suspended colloids within fractured and granular material occurs because of two types of phenomena: (1) physical effects, and (2) surface chemical effects. Physical filtration of colloids generally means the retention of colloids moving with the suspending fluid in pores, channels, and fracture apertures that are too small or dry to allow passage of the colloids. Two types of physical filtration are recognized in the unsaturated areas (Wan and Tokunaga 1997): conventional straining and film straining. Conventional straining, sieving, and pore-clogging will filter colloids if they are between 5 and 10 percent of

the size of grains in the media and thus likely larger than a pore throat diameter or fracture aperture. Where water saturation is low, colloids may be filtered by film straining if their size is greater than the thickness of the adsorbed water film coating the grains of the rock. The rate of colloid transport through thin water films depends upon the colloid size relative to the film thickness. Therefore, physical straining because of low saturation and surface chemical effects such as adhesion and flocculation through chance interception and diffusion will dominate. However, these processes are more important in the extensive unsaturated and saturated zones. Within the waste package, the filtration process is implicitly included in the colloid generation source term.

Colloid Sorption at the Air–Water Interface—Both hydrophilic and hydrophobic colloids may be sorbed at the gas–water interface for partially saturated conditions (Wan and Wilson 1994). Similar to physical straining at low saturation, the concentration of colloids sorbed depends on the saturation degree. However, other factors include the affinity of colloids for the gas–water interface, the electrostatic charge, and the salinity of the aqueous phase (BSC 2003f, Section 5.7). Hydrophobic colloids have higher affinities for the air–water interface. Colloids with low negative charge exhibit a stronger affinity. Also, high salinity of the aqueous phase generally promotes sorption. Buck et al. (2003) found that hydrophobic colloids of meta-studtite and meta-schoepite generated from degradation of CSNF tend to irreversibly attach to the air–water interface. These colloids contain moderate levels of neptunium and plutonium as well as high levels of strontium, cesium, and technetium. Colloid sorption to stationary air–water interfaces generally retard colloid transport, except in cases of relatively high saturation where bubbles with attached colloids could be transported. However, high-saturation conditions are expected to be unlikely in the drift and the unsaturated zone. Therefore, within the waste package, the colloid sorption at the air–water interface is not considered in the colloid generated source term.

3.2 MODELING ASSUMPTIONS

3.2.1 Colloids from the Corrosion of Commercial and DOE Spent Nuclear Fuel

Long-term corrosion testing of CSNF and DSNF under unsaturated, oxidizing conditions has been performed to examine the release of dissolved radionuclides, as well as radionuclides associated with colloids (BSC 2003f). Testing was designed to simulate a variety of Yucca Mountain repository relevant water-exposure conditions for several spent nuclear fuels with a range of fuel burnup and composition. Results from the unsaturated testing of CSNF and DSNF at Argonne National Laboratory indicated formation of alteration products containing very low concentrations of uranium-based colloids and dissolution of the uranium-based colloids in less than several months (BSC 2003f, Section 6.3.1.2). Uranium-based spent nuclear fuels will be prevalent in the repository, and the colloidal properties of a mixture of two uranium minerals, meta-schoepite $[(\text{UO}_2)_4(\text{OH})_6 \cdot 5\text{H}_2\text{O}]$ and UO_{2+x} , have been examined (BSC 2003f, Section 6.3.1.2.3). These colloids are stable under short duration tests with respect to dissolution and interparticle interactions at near neutral and higher pH values in solutions saturated with the respective mineral phases. Furthermore, these colloids dissolve after introduction to J-13 groundwater in short duration tests. Natural analog studies also suggest that colloidal uranium will not be a significant contributor to radionuclide transport under oxic pH-neutral environments

in uranium deposits (BSC 2003f, Section 6.3.1.2.4). Thus, colloids from CSNF and DSNF were eliminated from further consideration in the colloid modeling and abstraction.

3.2.1.1 Commercial Spent Nuclear Fuel

Assessment of the importance of potential colloid formation from CSNF is based on four major observations: (1) very low colloid concentrations were observed in the CSNF degradation tests, at least an order of magnitude less than concentrations observed in the defense high-level radioactive waste glass degradation tests (based on dynamic light-scattering measurements) (Mertz et al. 2003); (2) the fraction of uranium in the colloid mass was uniformly low in the CSNF tests, the only deviation from this occurring immediately following one of two changes in vessel configuration in which the uranium fraction increased but rapidly decreased to the approximate level of earlier values (Mertz et al. 2003); (3) suspensions of meta-schoepite and UO_{2+x} colloids in J-13 groundwater appear to dissolve in short-term saturated tests (their stability in unsaturated solutions has not been tested (Mertz et al. 2003)); and (4) field studies at uranium-bearing deposits indicate generally that under oxidizing conditions at near-neutral pH, colloid particles contain little uranium, and there is little sorption of uranium complexes to colloids (BSC 2003f).

One of the reasons hypothesized for the low colloid release in the CSNF tests was the test configuration in which the Zircaloy-4 support for the fuel fragments had 7-micron holes. However, the results from the unirradiated UO_2 tests also show few colloids after the formation of alteration products (Wronkiewicz et al. 1997). The unsaturated tests on unirradiated UO_2 had a test configuration with large 2 to 3 mm holes at the holder base allowing for the spallation of UO_{2+x} particulate during initial corrosion. However, the formation of a dense mat of alteration products during the UO_2 corrosion apparently reduced particulate release by trapping particulate in the altered products (Wronkiewicz et al. 1997). A similar mechanism whereby the alteration products minimize particulate release may be applicable to the CSNF unsaturated tests.

The concentration of released particulates or colloids from the CSNF tests is very low except during movement of the fuel samples from one setup to another (Mertz et al. 2003). In that case, colloid and particulate concentrations increased temporarily but returned to very low concentrations after the disruption (Mertz et al. 2003). While this indicates that disruptive events may contribute to the release of particulates and colloids from CSNF, it also indicates that the longevity of the colloids in the leachate is very short relative to the regulatory period.

3.2.1.2 DOE Spent Nuclear Fuel

Of the approximately 250 different types of fuel in the DSNF inventory, metallic uranium fuel comprises approximately 85 percent (by weight of heavy metal) of that inventory and, as the only waste form in significant quantities distinct from the other spent fuel types, was selected for corrosion testing. An irradiated uranium metal fuel from the N-Reactor at Hanford was tested in an experimental setup similar to that used at Argonne National Laboratory for testing CSNF. Additional details on the testing can be found elsewhere (DTN: MO0306ANLSF001.459). Corrosion testing of metallic uranium samples resulted in rapid oxidization (within a few months) of the uranium primarily to an oxide sludge consisting of UO_2 and higher oxides of uranium (DTN: MO0306ANLSF001.459). Although the uranium fuel disintegrated rapidly,

corrosion testing was continued to determine the effect of groundwater leaching on the fuel sludge. Results from the corrosion tests showed that the composition of the DSNF colloids evolve over time from an initially UO_2 -rich population, to a mixed colloid population containing UO_2 and higher oxides of uranium as well as smectite clays, to a population that appears to be dominated by uranium-containing smectite clays.

After approximately one year of testing, the total quantity of uranium in the sludge represented approximately all the original uranium fuel sample. The uranium associated with the colloids corresponds to 0.002 to 0.006 weight percent of the original uranium fuel sample. The quantity of uranium in the fraction attached to the stainless steel vessel was 0.1 to 0.3 weight percent of the original fuel sample (DTN: MO0306ANLSF001.459). The attached material is measured by washing the stainless steel vessel in HNO_3 ; the attached material includes sorbed solutes, sorbed colloids, and precipitates (DTN: MO0306ANLSF001.459).

During DSNF corrosion, plutonium is predominantly associated with the colloidal, particulate, and sorbed size fractions. The $^{239}\text{Pu}/^{238}\text{U}$ ratios in the colloid fraction are significantly larger than those in the other fractions (sorbed, particulate, and dissolved) and is the only fraction that showed enrichment of plutonium in comparison to that in the fuel prior to corrosion (DTN: MO0306ANLSF001.459). Results from the testing suggest that plutonium is significantly adsorbed to the surface of colloids (such as corrosion products of the waste package or groundwater clays). However, it does not form as an embedded radionuclide in waste form colloids (DTN: MO0306ANLSF001.459).

3.2.2 Filtration of Colloids

Near the waste, colloids may form at corroded waste fuel pellets and at its outer surfaces. They could be filtered within fractures in fuel pellets or trapped at grain boundaries. Colloids forming within fuel rods whose cladding has been breached could be filtered at perforations in the cladding. Colloids formed and spalled from the defense high-level radioactive waste glass could be filtered at perforations in the stainless steel high-level radioactive waste canister. No differentiation was made between colloid filtration and generation in the waste degradation experiments. Physical and chemical filtration of colloids is thus implicitly part of the generation process of colloids for radioactive waste. This filtration is a possible reason for the observed lack of waste form colloids in leachate leaving the CSNF and DSNF degradation experiments at Argonne National Laboratory noted above in Sections 3.2.1.1 and 3.2.1.2.

Colloids reaching the interior of the waste package (after escaping from fuel-rod cladding and high-level radioactive waste containers) could be filtered at perforations in the skin of the waste package. However, further filtration within the waste package and the drift is excluded from modeling. There have been no comprehensive studies of colloid filtration within the defense high-level radioactive waste glass. Hence, meaningful analysis of colloid filtration separate from colloid generation within the waste package is currently not feasible. Therefore, a conservative assumption is made: all colloids formed within the waste (the calculated colloid source term) are assumed to exit the waste package and invert (see Section 4 for a discussion of the invert) and enter the unsaturated zone without filtration (BSC 2003f).

3.2.3 Microbes and Colloidal Organic Components

The occurrence of microbes in the repository has been evaluated in *In-Drift Microbial Communities* (CRWMS M&O 2000a). In assessing the potential effects on microbial populations within the engineered barrier system, *In-Drift Microbial Communities* (CRWMS M&O 2000a) considered the drift mineralogy; drift physical parameters; metals, alloys, and cement used in engineered barrier system components; waste dissolution rates and quantities; groundwater compositions and infiltration rates; and compositions and fluxes of gases (e.g., CO₂, water vapor). Environmental limits on microbial activity considered include redox conditions, temperature, radiation, hydrostatic pressure, water activity, pH, salinity, available nutrients, and others. The abundance of water and phosphorous were found to be the two environmental components which, could limit the development of microbial communities in the Yucca Mountain repository under the probable physicochemical conditions likely to be present in the proposed repository configuration. However, water and phosphorous in the repository would potentially be available in sufficient quantities to allow for the growth of microbial communities at certain stages of the postclosure period (CRWMS M&O 2000a).

Microbes can accelerate or retard the transport of radionuclides in a number of ways. First, in some systems, microbes can passively or actively bioaccumulate radionuclides across the cell membrane. If the microbes are mobile, they can facilitate transport of the radionuclides. Alternatively, the microbes may be readily filtered by the rock or may form biofilms, a part of biomass attached to rocks, in which case they retard transport. Second, microbes may produce exudates, for example organic complexants, which may enhance the solubility of radionuclides and affect their sorption characteristics if complexes are formed. Third, in the course of extracting energy or nutrients, microbes may generate colloids by degrading materials or may actually destroy colloids by consuming them or by facilitating agglomeration. For example, microbial oxidation of metallic iron can produce iron-oxide colloids and aggregates. Conversely, microorganisms can decrease the concentration of stable colloids by aggregating colloidal material that they use as a food source. This has been shown to result in a significant decrease in colloid concentrations (Hersman 1995). Fourth, in some systems, microbes are able to reduce the oxidation states of some multivalent radioelements (e.g., uranium, neptunium, and plutonium). Typically, reduced forms of radionuclides are less soluble and more strongly sorptive. They may also impact local groundwater chemistry in and around the waste package.

Microbes and inorganic colloids in close proximity to one another may result in collisions, which allow mutual adhesion or adsorption and result in particle size growth (agglomeration) (Buffle et al. 1998; Hersman 1995). This increase in particle size can have several effects on the potential for colloids to facilitate radionuclide transport within the repository: (1) for a given range of pore sizes in the transport medium, the larger composite particles may become filtered more readily than the individual microbe or colloid; (2) the larger particles will tend to diffuse more slowly and/or may precipitate through gravitational settling; and (3) the interactions of relatively large populations of colloids and microbes can result in agglomerated particles sufficiently large that the suspension becomes unstable and the microbe and colloid particles flocculate. Reduced transport from increased particle size is even more significant in the situation where water is present as thin films within the pore spaces and on the engineered barrier system components. In all of these processes, the net result is particle size increase and reduced transport of colloids and associated radionuclides. Hersman (1995) conducted experiments with

Yucca Mountain-native bacteria and bentonite clay. In one test, agglomeration of clay colloids in a sterile microbial growth medium was compared to agglomeration in a medium into which a bacterium was introduced. The test results showed greater agglomeration in the growth medium inoculated with bacteria. In a second test, the bacteria were cultured in the medium and the test repeated with those bacteria, and similar results were noted.

The development of biofilms on a substrate has been shown to result in an increased tendency to attract suspended inorganic colloids. Sprouse and Rittmann (1990) and Rittmann and Wirtel (1991) demonstrated that biofilm colonization increased the colloid cohesion efficiency, α , in a system where the collector was granular activated carbon in a methanogenic fluidized bed and the colloids were milk solids approximately one micron in diameter. Lo et al. (1996) concluded from an experiment with Fe(III) oxide colloids in a biofilm reactor that the deposition of Fe(III) oxide colloids increased slightly with biofilms present. Further iron deposition on surfaces increased with increasing particle size, suggesting interception of the colloids and/or sedimentation.

Although uncertainty surrounds the microbial effect, the experiments with bacteria suggest that microbial action will tend to increase the sizes of inorganic colloids, and promote gravitational settling and filtration. Thus, not including the effects of microbes in the colloid source term and transport analysis is considered conservative with respect to total system performance.

3.2.4 Intrinsic Colloids

Intrinsic colloids are colloidal-sized assemblages (between approximately 1 nm and 1 μ m in longest dimension) formed from the hydrolysis and polymerization of actinide ions dissolved in solution (BSC 2003f). They may form in the waste package and engineered barrier system during waste-form degradation and radionuclide transport. Intrinsic colloids are also called primary colloids, Type I colloids, Eigenkolloide, real colloids, and true colloids.

The formation of intrinsic colloids is solubility limited and, thus, based on the solution chemistry. This fact prevents significant introduction of intrinsic colloids to the environment (CRWMS M&O 2001a, Section 6.1). There has been no evidence of their formation in Argonne National Laboratory defense high-level radioactive waste glass degradation tests (Ebert 1995, Sections 6.2.1 and 6.2.2). Degradation of CSNF may form intrinsic colloids (e.g., schoepite-like uranium hydroxides) close to the fuel surface where the fluid may be saturated with respect to uranium, but they are likely to dissolve in unsaturated fluid. Because experimental data supports the conclusion that intrinsic colloids are negligible, intrinsic colloids are not considered in the TSPA-LA.

3.2.5 Effect of Temperature on Colloids

Coupled thermal, hydrologic, and chemical effects are likely to result in unstable colloid suspension and, therefore, reduce the number concentration of colloids in suspension. With increasing temperature and increasing ionic strength, both conditions expected as a result of thermal, hydrologic, and chemical effects, colloid suspensions become less stable. Specifically, the coupled thermal-chemical perturbation will take place in the first few thousand years after repository closure (Figure 3-2). The thermal event produced by radiation heat will create a

drying-out zone and induce water evaporation within the drift and the surrounding area, resulting in the increase in the ionic strength in the percolating solution. The chemical degradation of waste package will further concentrate the solution (Figure 3-4). The increase in ionic strength will reduce the stability of both smectite and iron oxyhydroxide colloids inside the drift.

For example, the rate of particle coagulation is described by the stability relationship, W , defined as (BSC 2003f):

$$W = \exp(V_{max}/kT) \quad (\text{Eq. 3-2})$$

where, V_{max} is the height of the energy barrier preventing particle coagulation; k is the Boltzman constant; and T is temperature. Thus, increasing the temperature will cause a colloid suspension to become less stable. This is because the elevated temperature will enhance Brownian motion of the particles and therefore increase the probability of interparticle collisions.

In addition, the thermal event and its induced chemical perturbations are limited in space and transient in time. Because of the drying-out effect, a significant release of radionuclides from waste packages can be possible only after the thermal event, when the coupled thermal-chemical perturbations become completely attenuated and enough seepage water becomes available for leaching radionuclides. It is possible that some chemical perturbations may result in an increase in colloid concentration. However, such perturbations are expected to be transient and will attenuate rapidly as the colloid suspension moves away from the disposal room.

This conclusion is consistent with the results reported by Triay et al. (1996) who found that, under the perturbed conditions expected at Yucca Mountain, colloid concentrations are unlikely to be high enough to effectively compete with the immobile rock for the sorption of radionuclides. High temperatures and high ionic strengths are not favorable to colloid transport. Therefore, the screening out of coupled thermal-hydrologic-chemical effects on the transport of radioactive colloids in the TSPA is a reasonable assumption.

3.2.6 Colloid Sorption at the Air–Water Interface

The concentration of colloids sorbed at the gas–water interface is a function of the following conditions (BSC 2003f, Section 5.7):

- The interface surface area available for colloid uptake, which is a function of the total gas saturation
- The affinity of colloids for the gas–water interface (hydrophobic colloids have higher affinities than hydrophilic colloids)
- The electrostatic charge on the colloid—colloids with lower negative charge exhibit a stronger affinity
- The salinity of the aqueous phase with higher salinity promoting sorption.

Empirical evidence suggests that the sorption affinity of colloids at the gas–water interface may be stronger than to the rock matrix (Wan and Wilson 1994).

Partially saturated conditions may be classified by considering degrees of saturation. At low water saturations, the surface area of the gas–water interface approximates that of the rock matrix. Overall, colloid migration is retarded, although colloids may still move through the adsorbed water films. At intermediate water saturations, there is still an interconnected gas phase, although gas flux may be lower. The interface may act as a static sorbing surface, but estimating the geometry and surface area is complicated. At high water saturations, the majority of the gas is present as small gas bubbles that may migrate, transporting sorbed colloids.

Colloid migration rates depend more strongly on colloid size as lower saturation states are considered (CRWMS M&O 2001b; McGraw 1996). To examine the influence of colloid size on transport, McGraw (1996) investigated transport of monodisperse colloids (five different sizes, between 20 nm and 1,900 nm) under both saturated and unsaturated conditions in a quartz sand. The results indicated that under saturated conditions the time required for breakthrough of 50 percent of the original colloid concentration was the same as that of the breakthrough of a nonreactive tracer, indicating no relationship of colloid size to migration under saturated conditions. However, the times required for breakthroughs of the colloids under highly unsaturated conditions exhibited a strong relationship between the colloid breakthrough and the colloid size with fairly complete breakthrough of the 20-nm colloid and little or no breakthrough of the 1,900-nm colloid.

Another set of experiments (McGraw 1996) compared four sets of hydrophobic and hydrophilic colloids (modified latex microspheres). The results indicated that transport of hydrophobic colloids depends on colloid size, water film thickness, and colloid charge density. In contrast, hydrophilic colloids were not affected by these variables and were rapidly transported through the system even under very low moisture contents. It was concluded that for hydrophobic colloids, the cumulative mass of colloids recovered relative to column input was logarithmically dependent upon the ratio of the water film thickness to colloid diameter. In contrast, for hydrophilic colloids, the cumulative mass of colloids recovered relative to the column input was linearly dependent upon the ratio of the water film thickness to colloid diameter; similar, but more pronounced than, the effect with the nonreactive tracer. These findings suggest that unsaturated porous media may not completely impede colloid migration when a water film is present, even for relatively large colloids, however, larger colloids will tend to be retarded more than smaller ones.

Although the potential effects of degree of saturation on colloid transport are varied and complex, on balance colloids would be somewhat retarded under low-saturation both inside and outside the waste package. Because of this conclusion, sorption at the air–water interface is conservatively omitted within the waste package.

3.2.7 Selection of Radioisotopes

Transport of radioisotopes on colloids is potentially important for radioisotopes that (1) have long half-life and low solubility; (2) can be entrained in, or sorbed onto, waste forms, engineered barrier materials, or geologic barrier materials that generate colloidal particles; (3) represent a major portion of the inventory; and (4) have large dose conversion factors. Considering these four criteria as part of radionuclide screening, *Waste Form and In-Drift Colloids-Associated Radionuclides Concentrations: Abstract and Summary* (BSC 2003f) evaluated eight

radionuclides for sorption onto colloids: plutonium, americium, thorium, cesium, protactinium, neptunium, uranium, and strontium. Considering these four criteria as part of radioisotope screening, the colloidal concentration abstraction concluded that five radioisotopes attached to colloids should be evaluated: plutonium, americium, thorium, cesium, and protactinium. Four of these were analyzed in TSPA for site recommendation (CRWMS M&O 2000b; Leigh and Rechar 2001). Cesium has been added for TSPA-LA based on an updated screening analysis (BSC 2003f). Plutonium, americium, thorium, cesium, protactinium are assumed to be attached to colloids reversibly using a linear isotherm model. Plutonium and americium are assumed to be predominantly attached to iron oxyhydroxide colloids and smectite waste form colloids irreversibly. The following discussion summarizes the rationale used to include or exclude these radionuclides from the model for reversible attachment to colloids (BSC 2003f, Section 6.3.3.1).

3.2.7.1 Rationale for Including Five Radioisotopes

Plutonium—Plutonium meets all four criteria. A large quantity of plutonium will exist in the repository (criterion 3). Plutonium is sparingly soluble (criterion 1) but sorbs strongly to oxide mineral surfaces (generally less strongly to silicates). Plutonium is observed to sorb strongly to soil mineral, and laboratory investigations have shown that it sorbs readily to colloids as well (criterion 2). Finally, plutonium has a large dose conversion factor.

Americium—Americium also meets all four criteria. Americium will be a significant contributor to radioactivity during the first 10,000 years. Like plutonium, americium is sparingly soluble but strongly sorbs to mineral surfaces, including colloids. Laboratory investigations have shown that it sorbs strongly to colloids.

Protactinium—Protactinium will be a significant contributor to radioactivity during the first 10,000 years. Because of this, and the fact that relatively little is known of the colloid behavior of protactinium, it was included in this analysis.

Thorium—Thorium will be a significant contributor to radioactivity during the first 10,000 years. Because of this, and the fact that there is evidence that thorium sorbs strongly to oxides, it was included in this analysis. There is relatively little known of the colloid-related behavior of thorium.

Cesium— ^{135}Cs has a long half-life and can attach strongly to certain sheet silicates (including clays) by means of ion exchange. For this reason, cesium has been observed to sorb to soil minerals, and it could potentially form pseudocolloids particularly with groundwater and defense high-level radioactive waste glass-derived clay colloids.

3.2.7.2 Rationale for Excluding Neptunium, Uranium, and Strontium

Neptunium—Because neptunium will be the most significant contributor to radioactivity beyond the first 10,000 years, it was considered for inclusion in this analysis. Neptunium is more soluble under anticipated repository conditions than many of the other important radionuclides, and it sorbs considerably less strongly than, for example, plutonium and americium (see Table 3-1). The typical K_d values for neptunium sorption on Yucca Mountain-vicinity colloids are less than 100 mL/g. As demonstrated in Section 3.5, as long as K_d is less than 5000 mL/g, colloid-facilitated transport is not likely to be significant relative to transport of dissolved

species. It would appear then that the mobility of neptunium is influenced mostly by its solubility. For these reasons, and to simplify the modeling, neptunium was not included in the reversible-sorption portion of the colloid-associated radionuclide transport analysis.

Uranium—Uranium will be by far the most abundant radioactive element in the repository and primarily for this reason was considered for the analysis. Uranium is more soluble under anticipated repository conditions than many of the other important radionuclides, and it sorbs considerably less strongly than, for example, plutonium and americium. K_d values for uranium sorption on Yucca Mountain-vicinity colloids typically are less than about 1,000 mL/g (Table 3-1). As demonstrated in Section 3.5, as long as K_d is less than 5,000 mL/g, colloid-facilitated transport should not be significant relative to transport of dissolved species. As with neptunium, the mobility of uranium is thus influenced mostly by its solubility. Field observations at uranium deposits and mine sites have indicated that little or no colloid uranium transport occurs. For these reasons, and to simplify modeling, uranium was not included in the reversible-sorption of the colloid-associated radionuclide transport analysis.”

Strontium—Because of its very short half-life, strontium was not considered important in the groundwater pathway either as a dissolved species or attached to colloids.

Table 3-1. Modeled K_d for Plutonium, Americium, Thorium, Neptunium, and Uranium Sorption onto Yucca Mountain-Vicinity Colloids

Radionuclide Sorbate and Oxidation States at YMP	K_d Values, mL/g
U(VI)	1 to 6×10^2
Np(V)	1×10^1 to 1×10^2
Pu(V)	1×10^3 to 1×10^4
Th(IV)	2×10^3 to 9×10^4
Am(III)	1×10^4 to 1×10^7

Source: BSC 2003f, Table 9.

3.2.7.3 Rationale for Irreversible Adsorption

Defense high-level radioactive waste glass degradation experiments show that plutonium is probably irreversibly attached to smectite colloids generated during the experiments. Further, evidence from sorption experiments with plutonium and americium (Lu et al. 2000) with colloidal hematite and goethite show that the rates of desorption (backward rate) of plutonium and americium are significantly slower than the rates of sorption (forward rate). More importantly, over a significant time period (up to 150 days in some experiments), the extent of desorption is considerably less than the extent of sorption. Plutonium and americium are considered so strongly sorbed to colloids that, in essence, they can be considered irreversibly sorbed and are modeled in this manner within the engineered barrier system. Plutonium transport velocities in soils reflect the fact that plutonium binds strongly to soils, leaving very little, if any, soluble plutonium available for groundwater transport or plant uptake. Coughtrey et al. (1985) estimate exchangeable plutonium to be less than one percent. At Rocky Flats, plutonium in soil is largely bound to soil metal hydroxides. Litaor and Ibrahim (1996) used 0.01M CaCl_2 as an extractant and measured plutonium in Rocky Flats soil to be 0.04 to 0.08 percent exchangeable. Bunzl et al. (1995) measured exchangeable ^{239}Pu and ^{240}Pu (0.5 to

1 percent) and ^{241}Am (1.5 to 15 percent) from fallout-contaminated soils in Germany using 1M $\text{C}_2\text{H}_7\text{NO}_2$ (ammonium acetate $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$) as the extractant. Laboratory experiments of plutonium sorption onto iron oxides have shown that only approximately one percent of the initially sorbed plutonium can be desorbed into solution, even after months of time have elapsed (Lu et al. 2000), which is broadly consistent with field observations. For these reasons, plutonium and americium are modeled as irreversibly attaching to corrosion (iron oxyhydroxide) colloids. No other radionuclides are considered to be irreversibly attached to colloids.

3.3 SOURCE OF DATA AND TESTING

3.3.1 Tests on Defense High-Level Radioactive Waste Glass

Tests on defense high-level radioactive waste in borosilicate glass have been conducted at Argonne National Laboratory using two modes of water contacting the waste (CRWMS M&O 2001a). In the static-saturated test, glass samples were immersed in fluid for more than four years. In the dripping tests, fluid was dripped at specified rates onto glass samples. Fluid used was J-13 water and deionized water. It was observed in the static-saturated tests that colloids developed and increased in concentration with time, up to the point where the colloid concentration reached a maximum value and then decreased (Figure 3-5). From Figure 3-5, it is estimated that 1×10^{-7} M plutonium is equivalent to 5 ppm of total radionuclide-embedded colloids when both concentrations reach their maximum values.

3.3.2 Tests of Waste Package Corrosion

Maximum colloid concentration values are estimated based on experiments performed at University of Nevada, Las Vegas. In these experiments, scaled-down miniature waste packages were exposed to J-13 groundwater in either a bathtub mode or a flow-through mode. The experimental results obtained indicate that the iron corrosion products are mainly composed of magnetite (Fe_3O_4), lepidocrocite (FeOOH), and goethite (FeOOH) (DTN: MO0302UCC034JC.003). The cumulative results have yielded average concentrations of colloidal size materials in the range of 20 mg/L within the initial four weeks of the experiments (DTN: MO0212UCC034JC.002).

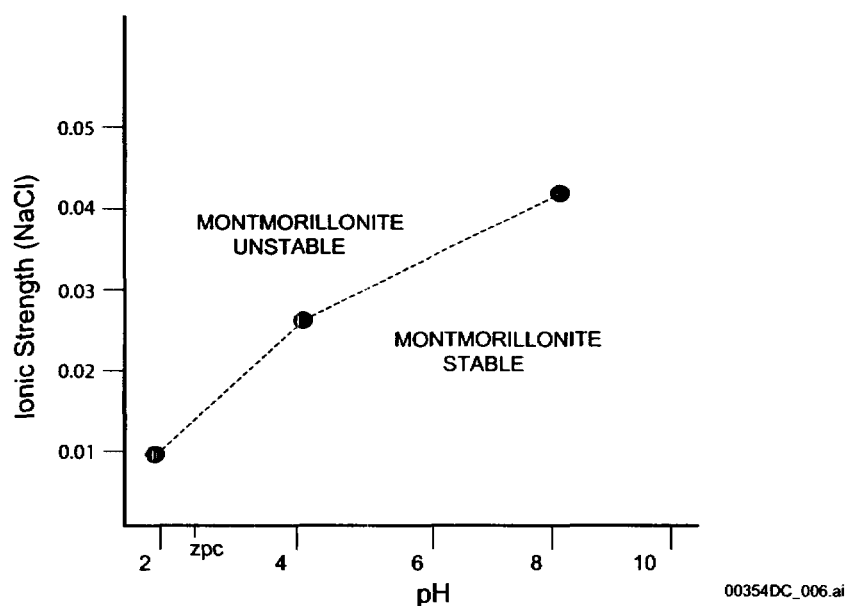
3.3.3 Iron Oxyhydroxide Colloids in Nature

Few data for iron oxyhydroxide colloids concentrations in nature have been found in the scientific literature, and the colloid concentrations reported vary greatly. At an iron rich ore body in South America, the Morro de Ferro natural analog site, the concentration was near 1 mg/L. Values ranging from 0.6 mg/L to 260 mg/L were measured in the vicinity of a mined uranium ore formation at Cigar Lake in Northern Saskatchewan (Vilks et al. 1993). Two Swedish groundwater colloid concentrations were measured to be 0.02 mg/L and 0.043 mg/L for saline and nonsaline groundwater samples, respectively (Laaksoharju et al. 1995). The experiments performed at University of Nevada, Las Vegas on miniature waste packages produced colloids ranging in concentration from near 0 mg/L to approximately 50 mg/L. As mentioned in Section 3.4, this latter information was used to define a uniform distribution between 0.05 and 50 mg/L.

3.3.4 Stability of Smectite and Iron Oxyhydroxide Colloids

The zero-point of charge of smectite is about pH 2 (Figure 3-6), below possible pH values anticipated within waste packages (BSC 2003h). Therefore, smectite colloids would remain stable if the ionic strength of the solution is low (less than 0.05 M). In the defense high-level radioactive waste glass tests conducted at Argonne National Laboratory, which were run at pH 9 and 11.5, smectite colloids were detected (Buck and Bates 1999). Tombacz et al. (1990) investigated the stability of smectite (also referred to as montmorillonite) suspensions as a function of pH and ionic strength in an NaCl solution. The results are summarized in Figure 3-6.

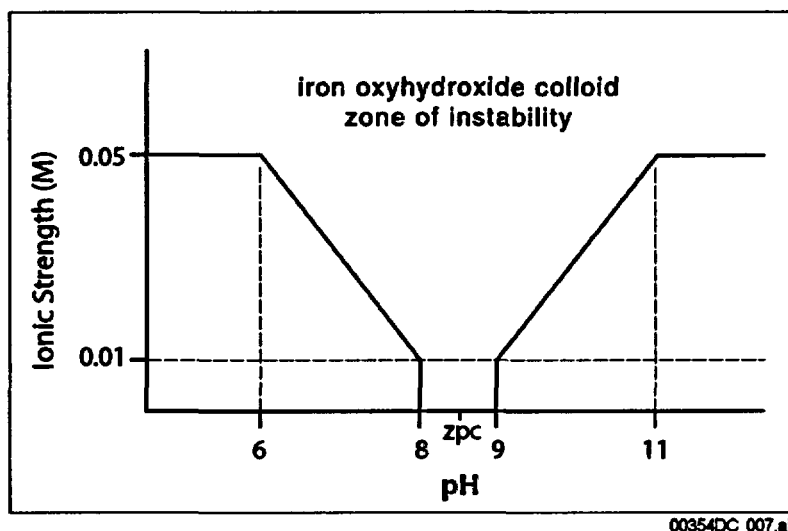
At a neutral pH, iron oxyhydroxide colloids tend to be unstable and agglomerate. The related stability diagram is displayed in Figure 3-7.



Source: BSC 2003f, Figure 4.

NOTE: zpc = zero-point of charge.

Figure 3-6. Experimental Determination of Montmorillonite (a Variety of Smectite) Stability as a Function of pH and Ionic Strength (M)



Source: BSC 2003f, Figure 7.

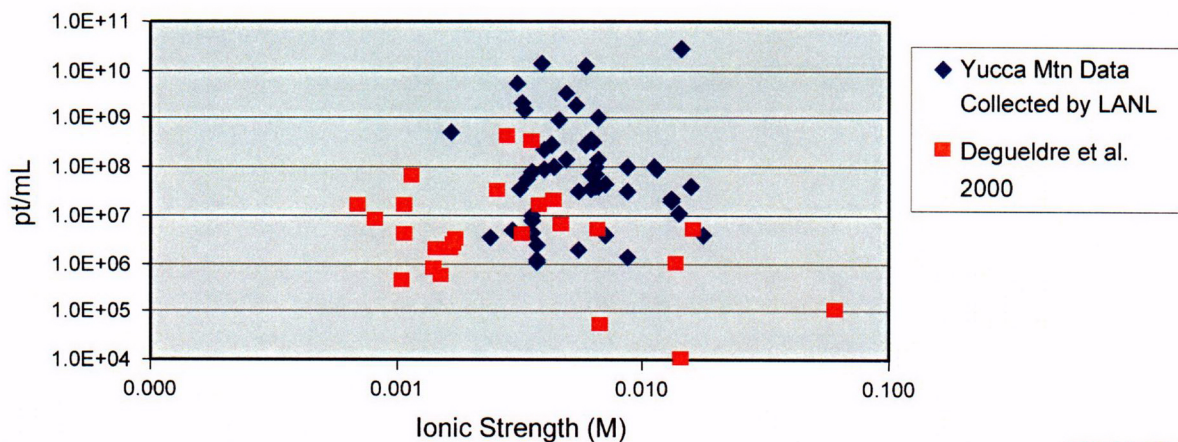
NOTE: zpc = zero-point of charge.

Figure 3-7. Schematic Representation of Iron Oxyhydroxide Colloid Stability as a Function of pH and Ionic Strength (M)

Note that the pH of groundwater at Yucca Mountain is generally close to neutral. Within this pH range, iron oxyhydroxide colloids would have a minimal surface charge, thus reducing mutual repulsive forces and resulting in flocculation, even at a low ionic strength. This fact explains why iron oxyhydroxide colloids may occur in low concentrations in groundwater and is one of the reasons why smectite colloids are used to represent seepage/groundwater colloids. This fact also implies that any iron oxyhydroxide colloids released from waste packages into groundwater may become unstable and flocculate as they move through the disposal system.

3.3.5 Colloid Concentrations in Groundwater

The range of colloid concentration in seepage/groundwater was derived based on groundwater sampling from the Yucca Mountain area. Literature data (Degueldre et al. 2000) and groundwater sampling at the Idaho National Engineering and Environmental Laboratory (BSC 2003f) was used as additional technical information that corroborated the site-specific data. The results are summarized in Figures 3-8 and 3-9. Practically no colloids were detected for the ionic strength above 0.05 M. The upper limit of colloid concentration is about 200 ppm, with a median value around 0.1 ppm (Figure 3-9).

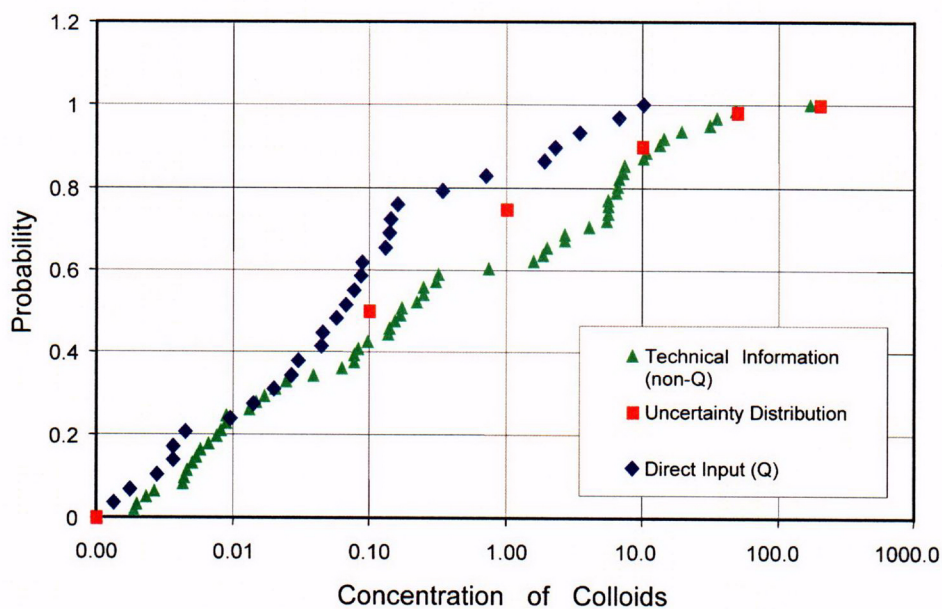


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Source: BSC 2003f, Figure 11.

NOTE: The ordinate values are in particles per milliliter (pt/mL).

Figure 3-8. Groundwater Colloid Concentration Data Collected in the Vicinity of Yucca Mountain Compared with Data Collected from Groundwaters around the World



00354DC_009.ai

Source: BSC 2003f, Figure 12.

Figure 3-9. Cumulative Distribution Function Showing the Probability of Occurrence of Colloid Concentration Levels (ppm or mg/L) in Groundwater Samples in the Yucca Mountain Area and Idaho National Engineering and Environmental Laboratory

3.3.6 Radionuclide Distribution Coefficients (K_d)

The effectiveness of colloid-facilitated transport depends on the sorptive affinity of radionuclides to a substrate, which can be described by the distribution coefficient (K_d) (Eq. 3-1). The K_d values used in the colloid transport modeling were obtained from various data sources and measurements including those from National Cooperative for the Disposal of Radioactive Waste (Switzerland), U.S. Environmental Protection Agency, and Yucca Mountain-specific projects (BSC 2003f). Based on these sources, professional judgment was used to develop uncertainty distributions (Table 3-2).

The work of Lu et al. (1998) needs to be mentioned specifically, because it provides the best direct evidence suggesting the irreversible sorption of plutonium onto colloidal particles. The work shows that Pu(IV) and Pu(V) were rapidly adsorbed by colloids of hematite, goethite, smectite, and silica in natural and synthetic groundwater. After five days, hematite colloids sorbed all Pu(IV) and Pu(V) present in the solution, goethite sorbed 97 to 100 percent of plutonium, smectite sorbed 94 to 100 percent plutonium, and silica sorbed 46 to 86 percent of plutonium. Desorption of plutonium from colloids of hematite, goethite, and smectite was much slower than the sorption process. After 150 days, less than 0.02 percent Pu(V) was desorbed from hematite colloids. Little colloidal Pu(IV) was desorbed from hematite colloids during 150 days, even using sequential extraction under vigorous shaking conditions. Although desorption of Pu(V), as well as Pu(IV), from goethite and smectite colloids is relatively faster, only less than 1 percent of plutonium was desorbed from goethite, and 1.5 percent Pu(V) and 2.5 percent to 11 percent of Pu(IV) were desorbed from smectite after 150 days.

3.4 MODEL FOR COLLOID-FACILITATED TRANSPORT IN WASTE PACKAGE

This section summarizes the algorithm used to incorporate the colloids source term abstraction in the TSPA-LA model, using a simplified model intended to retain the important principles and processes of the analyses. The logic implemented in the TSPA-LA model is provided, although specific programming details are not.

Table 3-2 K_d Values Used for Reversible Radionuclide Sorption on Colloids in Calculations for the Total System Performance Assessment for the License Application

Radionuclide	Colloid	K_d Value Range (mL/g)	K_d Value Intervals (mL/g)	K_d Value Interval Probabilities
Pu	Iron Oxyhydroxide	10^4 to 10^6	$<1 \times 10^4$ 1×10^4 to 5×10^4 5×10^4 to 1×10^5 1×10^5 to 5×10^5 5×10^5 to 1×10^6 $>1 \times 10^6$	0 0.15 0.2 0.5 0.15 0
	Smectite	10^3 to 10^6	$<1 \times 10^3$ 1×10^3 to 5×10^3 5×10^3 to 1×10^4 1×10^4 to 5×10^4 5×10^4 to 1×10^5 1×10^5 to 5×10^5 5×10^5 to 1×10^6 $>1 \times 10^6$	0 0.04 0.08 0.25 0.2 0.35 0.08 0
Am, Th, Pa	Iron Oxyhydroxide	10^5 to 10^7	$<1 \times 10^5$ 1×10^5 to 5×10^5 5×10^5 to 1×10^6 1×10^6 to 5×10^6 5×10^6 to 1×10^7 $>1 \times 10^7$	0 0.15 0.2 0.55 0.1 0
	Smectite	10^4 to 10^7	$<1 \times 10^4$ 1×10^4 to 5×10^4 5×10^4 to 1×10^5 1×10^5 to 5×10^5 5×10^5 to 1×10^6 1×10^6 to 5×10^6 5×10^6 to 1×10^7 $>1 \times 10^7$	0 0.07 0.1 0.23 0.2 0.32 0.08 0
Cs	Iron Oxyhydroxide	10^1 to 10^3	$<1 \times 10^1$ 1×10^1 to 5×10^1 5×10^1 to 1×10^2 1×10^2 to 5×10^2 5×10^2 to 1×10^3 $>1 \times 10^3$	0 0.13 0.22 0.55 0.1 0
	Smectite	10^2 to 10^4	$<1 \times 10^2$ 1×10^2 to 5×10^2 5×10^2 to 1×10^3 1×10^3 to 5×10^3 5×10^3 to 1×10^4 $>1 \times 10^4$	0 0.2 0.25 0.5 0.05 0

Source: BSC 2003f, Table 10.

NOTE: The K_d values for Tc and I are very low and not listed here.

3.4.1 Sources of Colloids

As already noted in Section 3.1, three sources of colloids are considered (Figure 3-10): (1) natural colloids in the seeping groundwater, (2) colloids generated from degradation of the waste package and other metallic materials in the repository, and (3) colloids generated from degradation of high-level radioactive waste. Colloids formed from the defense high-level radioactive waste glass and the naturally occurring groundwater colloids are represented by smectite colloids as explained in Sections 3.3.1 and 3.3.5. The three colloid types can transport reversibly sorbed radioisotopes, but plutonium and americium radioisotopes attached on iron oxyhydroxides colloids can also transport as “irreversibly” attached radioisotopes (Figure 3-10). Furthermore, colloids generated from spallation of the high-level radioactive waste glass have plutonium and americium radioisotopes engulfed during formation and are thus irreversibly attached as well. The colloidal concentration model uses concepts developed for the Compliance Certification Application for the Waste Isolation Pilot Plant (DOE 1996; Larson 2000; Stockman et al. 2000), in particular, categories of colloids tracked, mode of radioisotope uptake, and colloid stability.

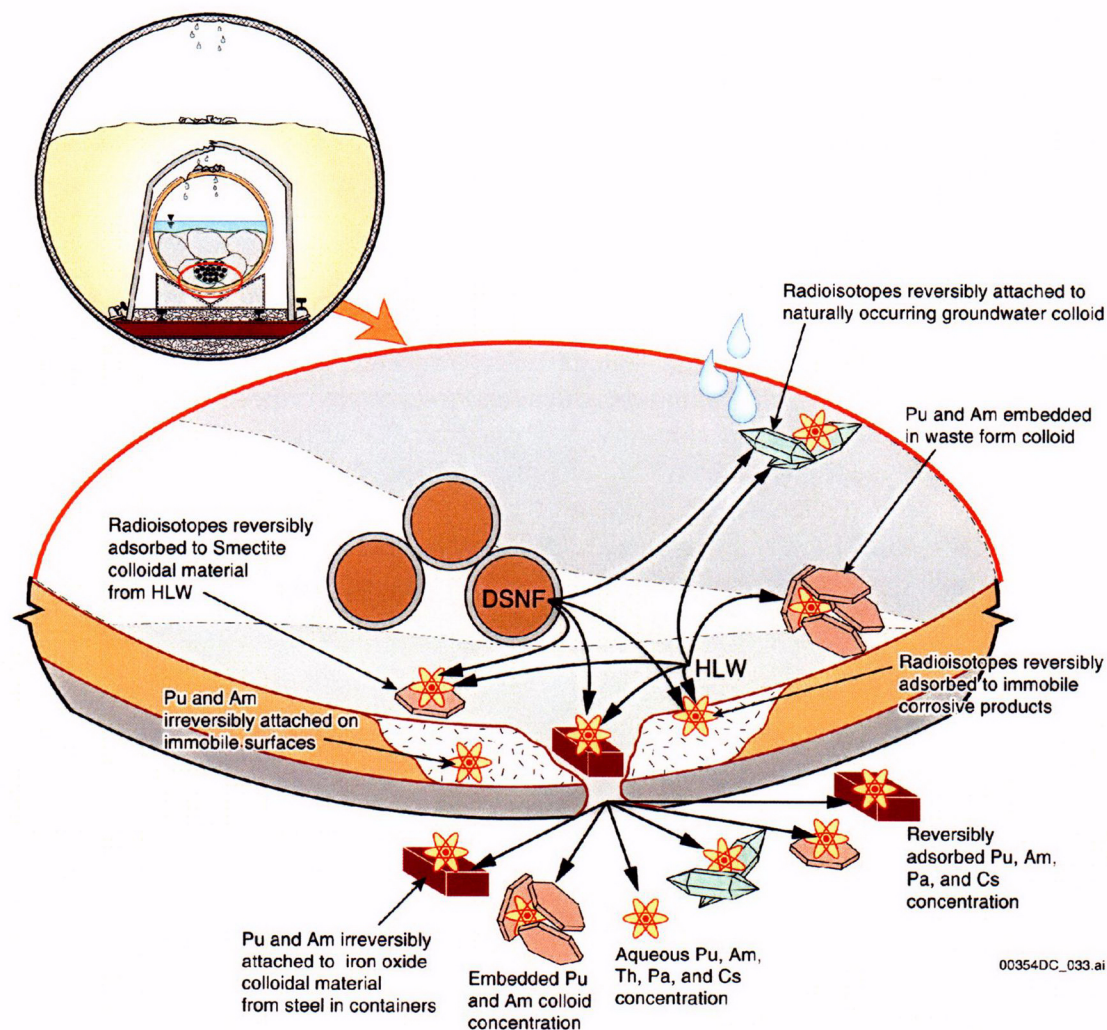


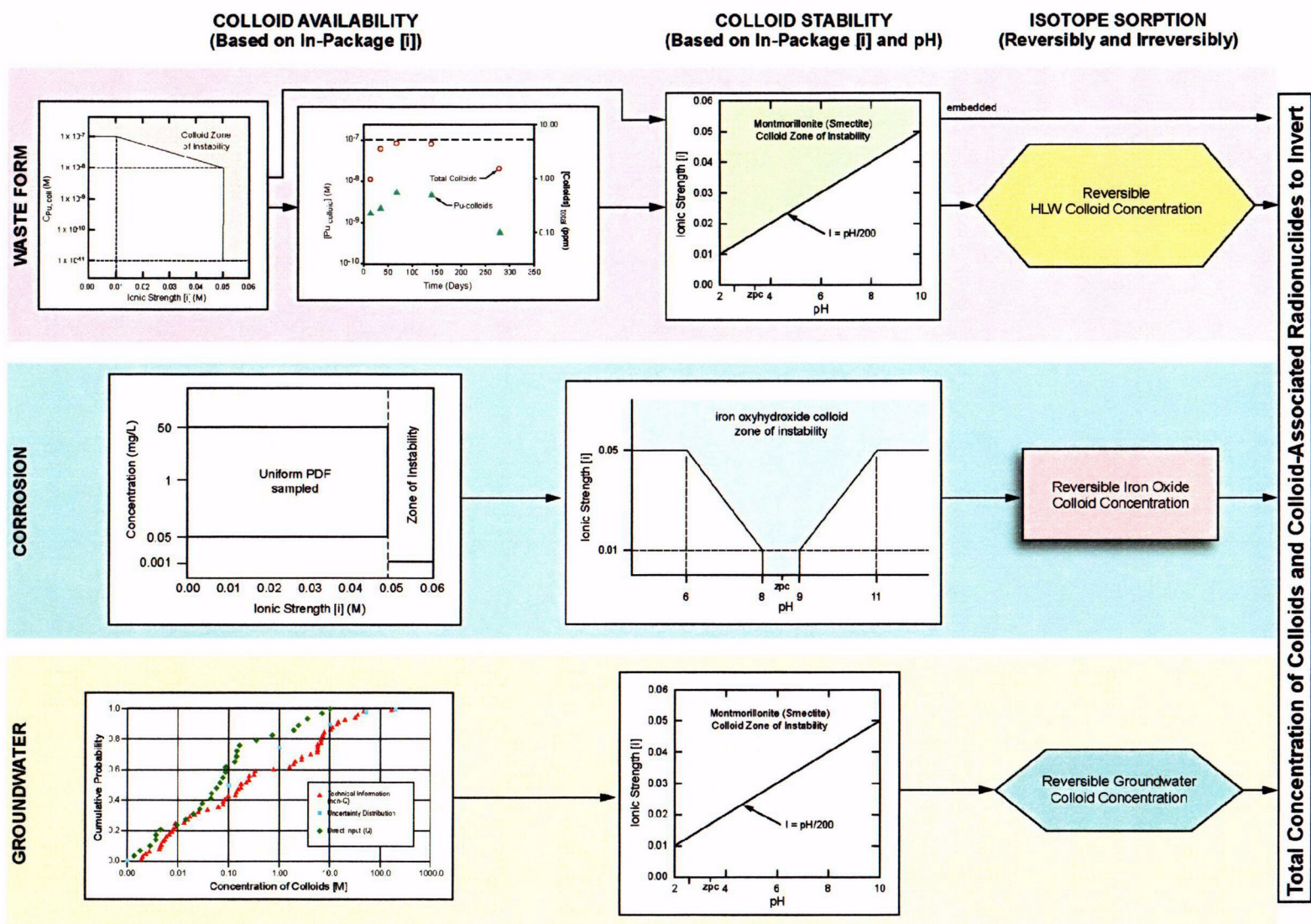
Figure 3-10. Embedded, Reversibly, and Irreversibly Attached Radioisotopes on Colloids

3.4.2 Algorithm Overview

The algorithm in the colloidal concentration abstraction for TSPA-LA consists of three steps (BSC 2003f) that are executed at each time step in the calculations (Figure 3-11). First, the component determines the potential colloidal mass available, usually as a function of ionic strength. Second, the component determines the stability of the colloidal mass as a function of ionic strength and pH, where ionic strength and pH are determined by the in-package chemistry (BSC 2003h) of the waste form model (CRWMS M&O 2000c; Rechard and Stockman 2001). When the colloids are unstable, a low (nonzero) limit of colloid concentration is used. Third, the component determines the fraction of the available mass of the dissolved inventory of cesium, americium, plutonium, protactinium, and thorium to be adsorbed onto the colloids. The dissolved inventory of the five radioisotopes is determined by the dissolved concentration component model (BSC 2003g) of the waste form model (CRWMS M&O 2000c; Rechard and Stockman 2001). The colloidal mass generated in Step 1 and its stability as a function of ionic strength and pH in Step 2 are generally bounding, but some uncertainty is included in parameter values for sorption in Step 3. The specific methods employed for these three steps depend on the source of the colloids. The description follows.

The abstraction calculates the concentration of dissolved radionuclides, the concentration of plutonium and americium embedded in defense high-level radioactive waste glass smectite colloids, the concentration of radionuclides sorbed reversibly onto the three colloid types, the concentration of radionuclides sorbed irreversibly onto iron-hydroxide colloids, and the mass concentration of each colloid type (Figure 3-11).

The colloidal concentration abstraction assumes that colloids are in the groundwater that enters a breached waste package and adsorb radioisotopes. Groundwater colloids potentially present in the repository include (1) microbes, (2) organic macromolecules (humic and fulvic acids), and (3) mineral colloids (primarily clay minerals, silica, and iron oxyhydroxide minerals). Microbial colloids were disregarded because the relatively large size of microbes makes them susceptible to filtration by the geologic media as already described in Section 3.2.3. Organic macromolecules were also disregarded, based on their low capacity to form chemical complexes at Yucca Mountain. Specifically, Minai et al. (1992) studied humic substances from J-13 well water and found that the complexation capacity was only about 2.3×10^{-10} eq/L (equivalents per liter) at pH 6.9 and 2.7×10^{-11} eq/L at pH 8.2, because of the presence of calcium in J-13 well water.



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Source: BSC 2003f, Figure 17a.

Figure 3-11. Algorithm for Determining the Availability and Stability of Colloids within the Waste Package

Mineral colloids were considered because quartz, feldspars, silica, cristobalite, fused silica, amorphous silica, aluminosilicates, layer silicates, zeolites, plagioclase, carbonate, smectite clay, hematite, and goethite colloids occur in groundwater in the vicinity of Yucca Mountain (Kingston and Whitbeck 1991). The mineral colloids were represented by smectite clays because smectite was the dominant colloid type observed and strongly adsorbs radioisotopes.

As discussed in Section 3.3, the YMP has compiled the colloid concentration in groundwater from igneous rock in saturated and unsaturated regimes from the vicinity of Yucca Mountain. This relationship was used for Step 1 of the procedure to estimate the groundwater colloidal mass concentration (Figures 3-9 and 3-11).

For Step 2, the colloidal concentration determined in Step 1 was maintained provided the pH and ionic strength were below the approximately linear stability function measured by Tombacz et al. (1990), based on known properties of smectite colloidal suspensions (Section 3.3.4, Figure 3-6). Otherwise, the colloidal concentration was reduced to a minimum value of 10^{-6} mg/L if ionic strength is less than 0.05 M. The threshold value of the ionic strength of the 0.05 M in the waste package used to calculate the concentration of groundwater colloids is identical to the upper threshold used for determining stability and concentration of waste form colloids, since both waste form and groundwater colloids are modeled as smectite.

To determine the mass of radioisotopes (plutonium, americium, thorium, protactinium, cesium) reversibly sorbed by the groundwater colloids for Step 3, a linear Freundlich model (Eq. 3-1) (Langmuir 1997) was used, using the dissolved concentration of radionuclides within the waste package as calculated by the solubility component of TSPA-LA model. The sorption coefficient (K_d) values for cesium, plutonium, and americium (and, by analogy, protactinium and thorium) were assigned piecewise uniform distributions, based on sorption experiments on smectite (Table 3-2). For cesium, the values range from 10^2 to 10^4 mL/g; plutonium ranged from 10^3 to 10^6 mL/g; for americium, the values range from 10^4 to 10^7 mL/g (Table 3-2).

3.4.3 Colloids from Iron Oxyhydroxide

The colloidal concentration component assumes that iron oxyhydroxide (rust) colloids (primarily goethite, ferrihydrite, and hematite) form during corrosion of waste packages. For Step 1, a uniform distribution was assigned with a range of 50 mg/L and 0.05 mg/L, based on the miniature colloid experiments conducted at University of Nevada, Las Vegas (Section 3.3.2).

For Step 2, the stability of iron oxyhydroxide colloids has been measured (Liang and Morgan 1990) and was used for developing the stability region as a function of pH and ionic strength. At and near the zero-point of charge, colloids are unstable, even at low ionic strengths. For iron oxyhydroxide colloids, the zero-point of charge ranges from about pH 5.5 to about pH 8.5 depending on the mineralogy and water chemistry. Colloids are stable at higher and lower pH values, similar to other mineral colloids, provided the ionic strength is less than 0.05 M. The result is a typical "U-shaped" stability curve (Figure 3-7). The minimum concentration of rust colloids in the unstable region was 10^{-3} mg/L.

For Step 3, two types of sorption are modeled, irreversible sorption of a large fraction of plutonium and americium onto iron oxyhydroxide corrosion colloids and fixed corrosion

products; and reversible sorption of a small fraction of plutonium and americium and reversible sorption of protactinium, thorium, and cesium onto iron oxyhydroxide colloids.

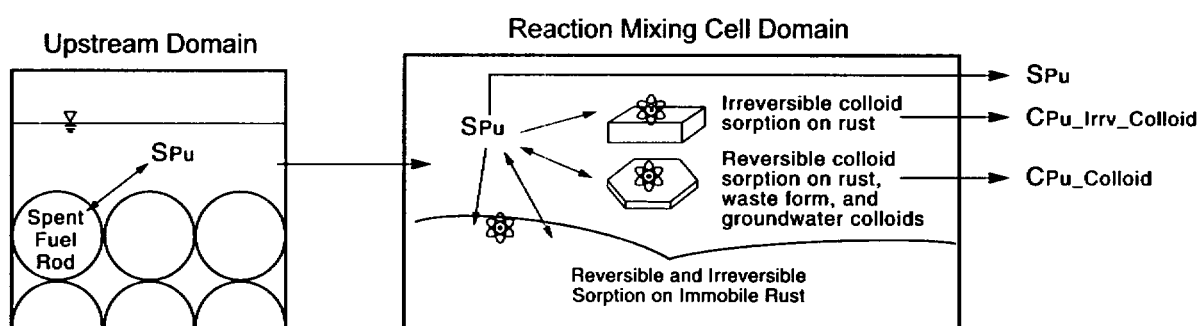
Plutonium and americium are considered so strongly sorbed to colloids that, in essence, can be considered irreversibly sorbed and are modeled in this manner within the engineered barrier system (BSC 2003o, Attachment II). Plutonium transport velocities in soils reflect the fact that plutonium binds strongly to soils, leaving very little, if any, soluble plutonium available for groundwater transport or plant uptake. Coughtrey et al. (1985) estimate exchangeable plutonium ("soil available," best estimate, Table 2a, p. 119) to be less than one percent. At Rocky Flats, soil plutonium is largely bound to soil metal hydroxides. Litaor and Ibrahim (1996) used 0.01M CaCl_2 as an extractant and measured plutonium in Rocky Flats soil to be 0.04 to 0.08 percent exchangeable. Bunzl et al. (1995) measured exchangeable $^{239+240}\text{Pu}$ (0.5 to 1 percent) and ^{241}Am (1.5 to 15 percent) from fallout-contaminated soils in Germany using 1M $\text{C}_2\text{H}_7\text{NO}_2$ (ammonium acetate $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$) as the extractant. Laboratory experiments of plutonium sorption onto iron oxides have shown that only about 1 percent of the initially sorbed plutonium can be desorbed into solution, even after five months of time have elapsed as already mentioned in Section 3.3.6 (Lu et al. 2000), which is broadly consistent with field observations.

In the colloid abstraction, the difference in specific surface areas between the colloids and the stationary corrosion products is taken into account as well as the total surface areas (based on total masses). For example, plutonium will tend to attach to the colloids with higher specific surface areas, while the much larger mass of stationary corrosion products relative to total colloid mass results in most of the dissolved plutonium attaching to the stationary corrosion products. Honeyman and Ranville (2002) incorporated a stationary phase in their analysis of the effects of colloids on radionuclide retardation. The stationary phase competes strongly with the colloids for radionuclide sorption. By far most of the americium mass was calculated as attached to the stationary phase; at most, 0.001 percent of the total americium was associated with colloids (Honeyman and Ranville 2002, p. 140). In order to accommodate the field and laboratory observations, distribution of plutonium between colloids and the stationary corrosion products was implemented such that a large fraction of total plutonium is sorbed to corrosion products, a small fraction to colloids, and a very small fraction remains dissolved in the fluid.

The distribution of irreversibly and reversibly sorbed plutonium and americium onto fixed and colloidal substrates is performed using a kinetic model that is described in *EBS Radionuclide Transport Abstraction* (BSC 2003o). Figure 3-12 shows the two domains of the conceptual model of radionuclide sorption onto the iron oxyhydroxide colloidal and stationary phases. The upstream domain is assumed to be degraded fuel rods, including secondary phases, in equilibrium with the aqueous phase at the radionuclide solubility limit (C_{RNdiss}) predicted by the solubility component (BSC 2003g). The radionuclides of concern are the plutonium and americium isotopes, but since the material balance equations are written as a mass balance, the equations are valid for any solute species. There is no sorption considered in the upstream

domain. Plutonium and americium are transported by both advection and diffusion downstream into the reaction mixing cell domain, where they can be involved in six¹ separate reactions:

1. Reversible plutonium and americium sorption onto iron oxyhydroxide colloidal particles
2. Reversible plutonium and americium sorption onto the stationary phase iron oxyhydroxide corrosion products
3. Irreversible plutonium and americium sorption onto iron oxyhydroxide colloidal particles
4. Irreversible plutonium and americium sorption onto the stationary phase iron oxyhydroxide corrosion products
5. Reversible plutonium and americium sorption onto waste form colloids
6. Reversible plutonium and americium sorption onto groundwater colloids.



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Note: SP_u refers to dissolved plutonium from spent fuel, other parameters as defined in figure.

Figure 3-12. First Two Computational Cells of Conceptual Model of Reversible and Irreversible Sorption on Mobile Iron Oxyhydroxide Colloids and Immobile Rust

The mass in the fluid exiting the reaction mixing cell is constrained such that the mass of plutonium sorbed both reversibly and irreversibly onto colloids is between 90 percent and 99 percent of the total mass of plutonium exiting the system in all forms—aqueous, reversibly sorbed, and irreversibly sorbed. This conforms to observations in nature, such as the transport of plutonium from the Benham test site (Kersting et al. 1999). This flux ratio is expressed as:

$$0.90 \leq \Omega = \frac{\text{colloid_mass_flux_out}}{\text{total_mass_flux_out}} \leq 0.99. \quad (\text{Eq. 3-3})$$

¹ Because plutonium and americium are also embedded into waste spalling from the high-level radioactive waste, they actually are involved in a total of eight separate reactions, but the embedded plutonium and americium are determined separately and not included in the kinetic model.

Also of interest is the ratio of the mass flux leaving the mixing cell to the mass flux entering the mixing cell. This ratio of mass out to mass in is given by

$$\Psi = \frac{\text{mass_flux_out}}{\text{mass_flux_in}} \quad (\text{Eq. 3-4})$$

and is a measure of the retardation due to the corrosion products. It is expected that most of the plutonium mass entering the mixing cell is sorbed to the stationary iron oxyhydroxide phase and only a small fraction of it flows downstream to the unsaturated zone.

Reversible sorption onto the colloids is calculated from the sampled mass concentration of corrosion colloids, K_d values between the fluid and iron oxyhydroxide colloids, and the dissolved concentration of radionuclides. The K_d values are defined with piecewise-uniform distribution describing the distribution of radionuclides (BSC 2003f, Table 10): the K_d for plutonium ranges between 10^4 and 10^6 mL/g. The K_d for americium, thorium, and protactinium ranges between 10^5 and 10^7 mL/g. The K_d for cesium ranges between 10^1 and 10^3 mL/g.

3.4.4 Colloids from High-Level Radioactive Waste

The laboratory evidence suggests that as high-level radioactive waste glass degrades, colloids are generated and often contain “embedded” or irreversibly attached plutonium and americium (CRWMS M&O 2001a). The embedded plutonium and americium are likely isolated from the aqueous system and thus not in equilibrium with the surrounding aqueous environment. Therefore, some plutonium or americium in the high-level radioactive waste is assumed to be embedded in the high-level radioactive waste colloids. On the other hand, few colloids have been observed in laboratory tests of CSNF, and those colloids observed did not have radioisotopes irreversibly attached (CRWMS M&O 2001a). Furthermore, DSNF is assumed to behave similarly to CSNF (Section 3.2.).

Step 1—For Step 1, colloidal concentration was set to a bounding value above the maximum value observed in the high-level radioactive waste experiments (1×10^{-7} M) at low ionic strength (CRWMS M&O 2001a). At ionic strength greater than 0.05 M, colloidal concentration was set at a low value (10^{-11} M). At intermediate ionic strength (between 0.01 and 0.05 M), irreversible colloidal concentration was calculated by interpolating between concentrations of 10^{-11} and 8×10^{-8} M.

Step 1a—The radionuclides plutonium and americium are modeled in Step 1a as embedded within waste form colloids, which are produced from corrosion of defense high-level radioactive waste glass. The concentrations are defined by ionic strength, based on experimental observations.

In TSPA-LA, $I_{hi-thresh, coll, wf}$ and $I_{lo-thresh, coll, wf}$ are threshold values of the ionic strength of the fluid in the waste package used to calculate the concentration of embedded plutonium used in the abstraction. Americium is calculated as the product of the plutonium concentration times the Am/Pu ratio in the inventory, which is determined at each time step of the TSPA-LA model calculations. Stability of the defense high-level radioactive waste glass-derived colloids is

determined in Step 1b. Colloid mass concentrations are calculated from the amount of plutonium embedded in smectite waste form colloids in Step 1c.

Step 1b—The stability of waste form colloids from defense high-level radioactive waste glass is determined on the basis of the fluid ionic strength and pH, based on known properties of smectite colloidal suspensions.

The $I_{hi-thresh, coll, wf}$ and $I_{lo-thresh, coll, wf}$ parameters are the same threshold values of the ionic strength of the fluid in the waste package used to determine plutonium concentration (Step 1a). They are used here to determine, along with pH, whether or not the colloids are stable. These threshold values may vary due to specific chemical and environmental conditions and are therefore sampled over a range.

Step 1c—Calculation of the mass concentration of waste form colloids from defense high-level radioactive waste glass is done on the basis of experimental observations.

The colloid mass concentration is related to the embedded plutonium concentration (Equation 3-3). With reference to Equation 3-3, $M_{coll, wf, both, max}$ is the maximum colloid mass concentration corresponding to the maximum plutonium concentration, $C_{RNcoll, wf, embed, max}$. It is an intermediate result based on the experimental data showing the relationship between embedded plutonium concentration and colloid mass concentration. $M_{coll, wf, both}$ is a parameter that represents the total mass concentration of defense high-level radioactive waste glass colloids with *both* embedded and reversibly sorbed radionuclides.

Step 1d—The calculation of the concentration of radionuclides (plutonium, americium, thorium, protactinium, cesium) reversibly sorbed on waste form colloids from defense high-level radioactive waste glass is based on the mass concentration of waste form colloids, K_d values describing the distribution of radionuclides between the fluid and smectite colloids, and the dissolved concentration of radionuclides as calculated by the TSPA-LA model.

The C_{RNdiss} is the concentration of radionuclide “RN”, determined by the TSPA-LA model as output from the solubility concentration model, which is used as an input to the colloid abstraction. $K_{d, RN, wf}$ is a parameter derived from several sources and is an equilibrium sorption coefficient used to approximate the partitioning of dissolved radionuclide “RN” between colloids and fluid.

Step 2—For Step 2, the simple linear stability relationship that was used for groundwater colloids (primarily smectite) was also used to determine the stability of the irreversible high-level radioactive waste colloid concentration as a function of pH because waste form colloids are composed primarily of smectite clay minerals (CRWMS M&O 2001a). When in the unstable region, the colloid concentration was set to 10^{-11} M.

Step 3—For Step 3, the algorithm is more complicated for high-level radioactive waste because the radioisotopes can be both irreversibly and reversibly attached to the high-level radioactive waste colloids. The algorithm makes several assumptions: (1) only americium and plutonium are irreversibly attached; (2) the irreversibly bound isotopes of plutonium and americium are partitioned according to the isotopic mass fraction calculated at the time the colloids are formed; (3) no initial mass of decay daughters are assumed irreversibly bound; and (4) in any one time

step, americium and plutonium do not attach reversibly until the maximum available mass of americium and plutonium in the high-level radioactive waste is irreversibly attached. That is, the concentration of irreversible americium and plutonium is first determined; then, the reversible available mass (including any available radioisotopes from DSNF) is calculated as the total mass available times the ratio of the irreversible concentration and the maximum irreversible concentration (Figure 3-11). The reversible concentration is determined with the linear Freundlich model. Both plutonium and americium used K_d values defined with piecewise-uniform distributions (Section 3.4.3).

3.5 UNCERTAINTY AND SENSITIVITY

3.5.1 Uncertainty of Colloid Concentration

The parameters developed for the colloid transport model have various degrees of uncertainty. The sources of uncertainty arise due to (1) uncertainty associated with the use of non-site-specific data in some cases to develop parameter values; (2) uncertainty associated with the prediction of actual physical and chemical conditions in the repository; (3) uncertainty associated with site- and environment-specific testing of colloid formation, stability, and transport; and (4) uncertainty associated with the use of supporting technical and corroborative information that may not have been developed specifically for these physical and chemical conditions. These uncertainties must be appropriately captured in the TSPA calculations by choosing conservative model formulations or appropriate upper/lower limits for parameter values.

In the implementation of a TSPA, it is often necessary to use experimental data gathered over a few days to a few years and field observations recorded over a few days to a few decades to arrive at conclusions on what is anticipated to occur over the 10,000-year regulatory compliance period. The parameters relating to irreversible association of radionuclides with colloids, which is influenced by kinetics, must be used cautiously when speculating about future conditions. Similarly, the extrapolation of laboratory-scale results to the scale of the repository setting also needs to be cautious. Corroboration with field data is generally required. Kersting et al. (1999) measured the total plutonium concentration at the ER-20 site, which is 1.3 km from the Nevada Test Site. The maximum plutonium concentration measured was about 10^{-14} M. Given the strong affinity of plutonium for solid surfaces, Kersting et al. (1999) argued that this low concentration indicated that a small fraction of plutonium could be potentially transported by colloids over a long distance. Whether this mechanism is plausible or relevant to the repository conditions (note that the physical/chemical conditions at Nevada Test Site can be very different from repository conditions), the low concentrations from Kersting et al. (1999) indicate that plutonium transported by groundwater can be attenuated very quickly over a short distance (~1.3 Km). The plutonium concentration was about six orders of magnitude lower than the solubility limits of 10^{-8} M experimentally determined as likely to be present in Nevada Test Site groundwater. Therefore, these observations indicate that there would be a potential for long-distance colloid-associated plutonium transport in the Yucca Mountain environment (given the fact that plutonium tends to be strongly sorbed on solid surfaces), but the contribution of such transport to system performance is unlikely to be significant.

Uncertainties associated with the determination of colloid concentration in seepage/groundwater derive from (1) field sampling techniques, including differences in pumping rates at each well

during extraction of the water samples, (2) other unknown factors affecting the quantities of particles suspended in the water samples, including the types of additives introduced in the wells during the drilling process itself, and (3) errors inherent to the laboratory methods used to measure the quantities of colloids suspended in the water samples (e.g., filter ripening, interference and detection limitations for dynamic light scattering measurement techniques). The sampling perturbation may result in over-estimating colloid concentrations.

With respect to the spatial scale, there is the issue of the appropriateness of extrapolation of specific water sample measurements to represent the colloid concentrations in waters over a wider region or area. Temporal scaling issues could include potential seasonal variations in the quantities of colloids suspended in water samples extracted, or even shorter time-scale changes in colloid concentrations in water samples during the sampling of wells. To define this uncertainty, a cumulative distribution function was developed based on groundwater samples extracted in the vicinity of Yucca Mountain (Section 3.3.5). To evaluate the reasonableness of this distribution for the site-specific data, the distribution function compared with colloid mass concentrations reported in the literature and at Idaho National Engineering and Environmental Laboratory (Figure 3-9). As shown in Figure 3-9, the probabilistic distribution of colloid concentrations developed for YMP is reasonable.

3.5.2 Uncertainty in Stability of Colloids

Uncertainty in the stability of colloids (smectite and iron oxyhydroxide) as a function of pH and ionic strength is associated mostly with the extrapolation of laboratory data reported in the literature or project-supported experimental work to actual conditions (i.e., solution chemistry) that would be present in the repository environment over the regulatory compliance period. Much of this uncertainty is accommodated by establishing conservative, but reasonable, bounding values and ranges of parameter values. This uncertainty is propagated through the TSPA-LA model by stochastic sampling of these distributions during Monte Carlo simulations employed in the model calculations.

3.5.3 Uncertainty in Partition Coefficients

Uncertainty is associated with the development of sorption partition coefficients (K_d values) to describe the degree of sorption of specific radionuclides to colloids. Values reported in the literature are primarily the result of experimental work designed to establish K_d values for contaminants sorbed onto rocks, soils and other minerals, but literature specific to colloid-size minerals is not readily available. For this reason, the K_d value parameters established for smectite and iron oxyhydroxide colloids rely on limited experimental work conducted at Los Alamos National Laboratory (Lu et al. 1998). Corroborative data reported in the literature were evaluated to augment the Los Alamos National Laboratory data (Table 3-2).

The transport of a radionuclide in the presence of a constant colloid concentration can be described by:

$$\frac{\partial(\phi m_d)}{\partial t} + \frac{\partial(\phi m_c)}{\partial t} + \frac{\partial[(1-\phi)\rho_s m_s]}{\partial t} = \frac{\partial}{\partial x} \left(\phi D \frac{\partial m_d}{\partial x} \right) + \frac{\partial}{\partial x} \left(\phi D \frac{\partial (m_c c)}{\partial x} \right) - \frac{\partial(\phi m_d V)}{\partial x} - \frac{\partial(\phi m_c c V)}{\partial x} \quad (\text{Eq. 3-5})$$

where ϕ is the porosity; m_d is the concentration of dissolved radionuclide (M); c is the colloid concentration (g/L); m_c is the moles of radionuclide sorbed on colloids (mol/g); ρ_s is the density of the immobilized adsorbing phase (g/dm³); m_s is the moles of radionuclide sorbed on the immobilized adsorbing phase (mol/g); V is the flow velocity (dm/y); D is the dispersion coefficient of the dissolved species (dm²/y); t is the time (y); and x is the spatial coordinate (dm). Substituting Equation 3-1 into Equation 3-5 for m_c , one can obtain:

$$\frac{\partial m_d}{\partial t} = \frac{\phi(1 + cK_d)D}{\phi(1 + cK_d) + (1 - \phi)\rho_s K_d} \frac{\partial^2 m_d}{\partial x^2} - \frac{\phi(1 + cK_d)V}{\phi(1 + cK_d) + (1 - \phi)\rho_s K_d} \frac{\partial m_d}{\partial x} \quad (\text{Eq. 3-6})$$

Therefore, the actual velocity of the advancement of the adsorption front (V') can be calculated by:

$$V' = \frac{\phi(1 + cK_d)}{\phi(1 + cK_d) + (1 - \phi)\rho_s K_d} V \quad (\text{Eq. 3-7})$$

Assuming that a fluid percolates through a porous medium of a length of L (dm), the total radionuclide release from the system over a time period T (y) can be approximately calculated by:

$$Q \approx \frac{AF}{V} \left[\frac{\phi(1 + cK_d)}{\phi(1 + cK_d) + (1 - \phi)\rho_s K_d} VT - L \right] \quad \text{for } V'T \geq L \quad (\text{Eq. 3-8})$$

where A is the cross-section area of the system; and F is the incoming flux (mol/dm²/y). For $V'T < L$, $Q = 0$, i.e., no radionuclide will be released from the system.

For the colloid-facilitated radionuclide transport to be negligible compared to the dissolved species transport, it is required that $cK_d \ll 1$. Using the upper colloid concentration limit of 200 ppm in the Yucca Mountain groundwater, it can be calculated that any radionuclide with a K_d less than 5,000 mL/g can be ignored for colloid-facilitated transport. These radionuclides include technetium, iodine, and cesium.

For $cK_d \gg 1$, Equation 3-8 is reduced to:

$$Q \approx \frac{AF}{V} \left[\frac{\phi c}{\phi c + (1 - \phi)\rho_s} VT - L \right] \quad \text{for } V'T \geq L \quad (\text{Eq. 3-9})$$

Therefore, as long as K_d is large enough (greater than 5000 mg/L), the total radionuclide release from the system becomes insensitive to K_d and only depends on the concentration ratio of colloids to the immobilized adsorbing phase, $\phi c / (1 - \phi)\rho_s$, which is typically very small.

3.6 MODEL CONFIDENCE BUILDING

Sensitivity studies conducted to prioritize work for the LA (BSC 2002a) showed that the colloids had a small effect on the dose. Therefore, a relatively low level of confidence is required for the colloid model.

The types and characteristics (including stability and concentration) of colloids formed from the degradation of the waste forms as used in the model abstraction is based on extensive observations of colloids from testing programs and natural groundwater.

The validation activities for this model analysis and abstraction took into account the criteria established in the *Yucca Mountain Review Plan, Final Report* (NRC 2003). Post-model-development validation is accomplished through corroboration of model predictions and data used with data published in referred journals or literature and through corroboration by comparison to data from natural analog sites. Detailed validation arguments are documented in *Waste Form and In-Drift Colloids-Associated Radionuclide Concentrations: Abstraction and Summary* (BSC 2003f). Corroborating/supporting data and information used to develop and validate the parameters are listed in Table 3-3. It is concluded that the validation activities performed for building confidence in the model elements and data developed for YMP colloidal transport have sufficient scientific basis and that the acceptance criteria documented in the *Yucca Mountain Review Plan, Final Report* (NRC 2003) will be met satisfactorily.

Table 3-3. Supporting (Corroborating) Information Used to Build Confidence in the Colloid Model

Supporting (Corroborating) Information Source	Data/Information
Tombacz et al. 1990	Stability of smectite (which is used as a surrogate mineralogy for defense high-level radioactive waste glass colloids) at full range of conditions anticipated in TSPA-LA calculations
Mertz et al. 2003	Corroborative data supporting conclusion of no significant colloids generated from CSNF degradation
Short et al. 1988	Corroborative information and data regarding low colloid-associated uranium concentrations in the vicinity of mines
Payne et al. 1992	Corroborative information and data regarding low colloid-associated uranium concentrations in the vicinity of mines
Zänker et al. 2000	Corroborative information and data regarding low colloid-associated uranium concentrations in the vicinity of mines
Vilks et al. 1993	Corroborative information and data regarding low colloid-associated uranium concentrations in the vicinity of mines
Brady et al. 2002	Corroborative information and data regarding limited extent of dissolved uranium plumes
DTN LA0002SK831352.003 DTN LA0002SK831352.004	Corroborative (non-Q) data for qualified groundwater data
Coughtrey et al. 1985	Corroborative information regarding irreversibility of plutonium on mineral particles
Litaor and Ibrahim 1996	Corroborative information regarding irreversibility of plutonium on mineral particles
Bunzl et al. 1995	Corroborative information regarding irreversibility of plutonium on mineral particles

3.7 SUMMARY

Three different types of colloids are considered in the modeling of the radionuclide source term:

- Waste-form colloids resulting from corrosion of defense high-level radioactive waste glass with embedded discrete phases of plutonium and americium and represented by smectite colloids
- Iron oxyhydroxide colloids resulting from the corrosion of waste package and metallic inert materials
- Natural colloids in seeping groundwater, including mineral fragments, humic substances and microbes and represented by smectite colloids.

Humic substances are not considered to be sufficiently abundant in Yucca Mountain groundwater to be of significant impact to radionuclide transport. Also, microbes, due to their relatively large size (about 1 μm) within the colloid-size range, are highly susceptible to filtration. Smectite colloids are used to represent natural colloids at the Yucca Mountain site, because of their abundance and relatively high affinity for radionuclides.

True or intrinsic colloids are eliminated from consideration in TSPA analyses for several reasons: (1) long-term corrosion testing with CSNF and DSNF under unsaturated, oxidizing conditions have shown very low colloid concentrations and small amounts of uranium within the colloid mass; and (2) the same test indicates that meta-schoepite and UO_{2+x} colloids readily dissolve upon the introduction of J-13 groundwater.

Defense high-level radioactive waste glass degradation experiments show that plutonium can be embedded in smectite colloids. Further, evidence from sorption experiments show that plutonium and americium are strongly adsorbed onto iron oxyhydroxide colloids and the rates of desorption of the two radionuclides are significantly slower than the rate of sorption. In the model it is assumed that over 90 percent of the adsorbed plutonium and americium is irreversibly adsorbed to both corrosion colloids and stationary corrosion products. The sorption of all other radionuclides is assumed to be reversible.

Colloid suspensions are likely to be unstable partly because of evaporation during the thermal period and waste degradation reactions may lead to ionic strengths above 0.05 M. For the seepage-water dripping scenario, the most relevant in-package chemistry scenario with regard to colloid transport, reaction-path calculations indicate that the initial seepage water composition is rapidly overtaken by water-package interactions (BSC 2003h). Depending on the seepage flux, as the chemical reaction progresses, the water can reach an ionic strength more than 0.05 M, the upper ionic-strength limit for stable colloid suspension. Therefore, under such conditions, colloid suspensions tend to be unstable.

Once formed and stably suspended, colloids could be filtered out. Notwithstanding the potential colloid filtration processes that would reduce the amount of radioactive colloids released from the waste package, it has been assumed that the waste package does not provide a barrier to the release of radioactive colloids. Therefore, the dominant mechanism leading to low

concentrations of colloids in suspension is the expected lack of stability of the colloids due to chemical conditions that lead to high ionic strengths.

4. INVERT

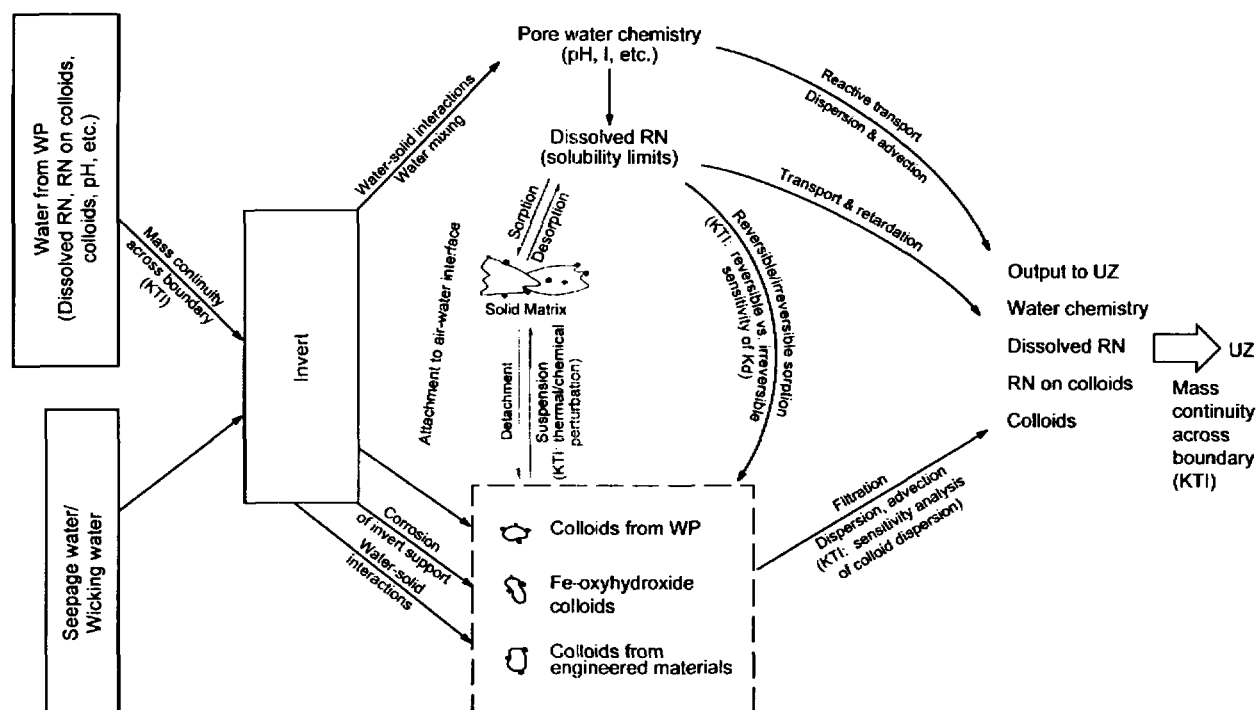
This section of the technical basis document summarizes the current understanding of the formation of radionuclide-carrying colloids within the invert and their release into the unsaturated zone. The invert is the second of the repository system subfeatures examined to determine the importance of colloids with respect to the postclosure performance of the Yucca Mountain repository system, as shown in Figure 1-1. This section provides a summary-level synthesis of the processes and phenomena governing the formation, prediction of their concentration, and transport of pseudocolloids within the invert. Modeling assumptions to be used in the TSPA-LA are discussed. In preparing this section, information has been extracted and summarized in pertinent analysis and model reports as well as other technical products that are used:

- *Multiscale Thermohydrologic Model* (BSC 2003n)
- *Advection Versus Diffusion in the Invert* (BSC 2003j)
- *EBS Radionuclide Transport Abstraction* (BSC 2003o)
- *Engineered Barrier System: Physical and Chemical Environment Model* (BSC 2003k).

4.1 DESCRIPTION OF RELEVANT PROCESSES AND MODELING ASSUMPTIONS FOR INVERT

4.1.1 Collapse of Pallet Supporting Waste Package

The invert, which is primarily composed of crushed tuff rocks, is 0.8 m thick. The relevant physical/chemical processes for colloid generation and transport in the invert are summarized in Figure 4-1. The waste package sits on a pallet composed of Alloy 22. The pallet, in turn, sits on an invert. Degradation of the pallet is not considered since it has been assumed to have collapsed by the time the waste package has breached. Hence, the waste package is assumed to be in intimate contact with the invert below. When releases of colloidal material are primarily through diffusion, as in the nominal case without any dripping seepage water, neglecting the pallet shortens the radionuclide transport path and, thus, is a conservative assumption as discussed in the feature, event, or process (FEP) screening-out argument for FEP 2.1.06.05.0A (BSC 2003o). In the following discussion, the invert also provides a large diffusion path for colloids in this situation as well. Either diffusion barrier by itself is probably sufficient to remove all colloids. Thus, it is necessary only to model one barrier. Because the pallet is reasonably omitted in the other two scenarios considered in the TSPA (the scenario where an igneous dike intrudes into the repository and the scenario where a seismic event severely shakes the repository), the pallet was not considered.



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Figure 4-1. Relevant Physical/Chemical Processes for Colloid Generation and Transport

4.1.2 Water Flow

All flux that may originate from the waste package flows to the invert, independent of patch/pit location on the waste package. The flux that is diverted around the waste package and the drip shield also flows into the invert. In addition, seepage water may also enter the invert by a wicking process. Finally, evaporation may take place in the upper portion of the invert during the thermal pulse over the first few thousand years after repository closure (BSC 2003o). Evaporated water may condense on the inside of the drip shield, and drip onto the waste package. All mass flux into the invert, except for the evaporative flux, is released into the unsaturated zone. During the regulatory period, the type of water flow through invert depends on the scenario under consideration (nominal, seismic, or volcanic), as explained further in Section 4.3.3. For the most part, the crushed tuff invert will maintain unsaturated conditions under the waste package and thereby reduce advective transport of colloids out of the engineered barrier (see Figure 3-2).

4.1.3 Invert Chemistry

Because of the generally slow seepage of water into the invert previously described, any seepage water entering the invert will have time to react with the crushed tuff. The resulting solution will tend toward neutral to mildly basic pH. Any seepage water entering the invert will combine with the flux from the waste package, and likely alter the chemistry of the flux from the waste package, as well. As a result, the iron oxyhydroxide colloids may become unstable (as shown in Figure 3-7). Also, the evaporation process may concentrate the solution, which may further

increase the instability of colloids in the invert. As explained further in Section 4.3.3, the chemistry of the water used in the invert was dependent on the scenario.

4.1.4 Generation of Additional Colloids

In addition to those colloids directly input from the waste package and the seepage water, similar colloids could be present in the invert and generated from the corrosion of pallet and steel supports within the invert. The corrosion of invert support material and electrical conductors will generate iron and copper oxides, which are generally strong adsorbents for various radionuclides. Although the mass of material in the drift including the steel mesh, ribs, invert support, and drip shield (~1.8 Mg/m) is about the same as in a CSNF waste package (~1.6 Mg/m), additional colloids present in the drift and the sorption effect were not included as important phenomena. First, the waste package material is in closer proximity to the actinides. Second, the spatial distribution of the corrosion products in the invert will tend to be localized and relatively widely spaced. Hence, seepage water from the waste package could completely miss corrosion products in the invert. Third, the iron oxyhydroxide colloids, representing the corrosion products, may be unstable in the invert water chemistry, as noted above. Finally, the additional sources are not expected to change the upper limits of colloid concentrations estimated in Section 3 from systems that have achieved metastable equilibrium states.

4.1.5 Colloidal Filtration

The extent of colloidal filtration cannot be expressed with certainty since physical properties of the crushed tuff have not been specified. Because of the large difference in colloid particle size and crushed tuff in the invert, physical filtration such as straining will likely be unimportant in the invert. Within the invert, the filtration process is not included because of the small dimension of the invert (0.8 m maximum) and, thus, limited opportunity for sufficient interaction of particles with the media. As an example of a model applied to nuclear waste disposal, Aguilar et al. (1999) modeled the filtration potential in an analysis for the performance assessment of the Waste Isolation Pilot Plant in Carlsbad, New Mexico. Their model predicted substantial filtration of colloids suspended in Waste Isolation Pilot Plant brines, often in distances of several meters. Based on typical parameter ranges and using a similar approach, Rechar et al. (2003) have shown that on average only minor filtration would occur in the invert due to the short filtration path of 0.8 m (maximum) and it has been ignored in the TSPA. However, filtration is modeled in the unsaturated and saturated zones in Sections 5 and 6, because of its greater extent.

4.2 SOURCE OF DATA AND TESTING

Diffusion coefficients used by the YMP for the invert material are tabulated in Table 4-1. Corroborative information is also available since the diffusion coefficient of ions has been determined specifically for crushed tuff invert materials as a function of volumetric moisture content (m^3 water/ m^3 bulk rock), using electric conductivity measurements (BSC 2003o, Table 41). The data are tabulated in Table 4-2. The diffusion coefficient for colloids is estimated from the Stokes-Einstein relationship (see Equation 4-1 in Section 4.3).

Table 4-1. Diffusion Coefficient for Granular Materials at Various Volumetric Moisture Contents

Volumetric Moisture Content (%)	Diffusion Coefficient (cm ² /s)
66.3	1.8×10^{-5}
49.0	6.09×10^{-6}
40.0	6.90×10^{-6}
32.3	4.60×10^{-6}
30.9	1.51×10^{-6}
20.4	4.19×10^{-6}
17.5	1.10×10^{-5}
10.1	3.51×10^{-7}
9.24	2.55×10^{-7}
5.40	7.60×10^{-8}
3.70	3.70×10^{-8}

Source: BSC 2003o, Table 6. DTN: MO0007MWDIDD31.001.

Table 4-2. Diffusion Coefficient of Crushed Tuff Invert Materials

Volumetric Moisture Content (%)	Diffusion Coefficient (cm ² /s)
32.13	2.02×10^{-6}
18.15	5.40×10^{-7}
9.26	4.05×10^{-8}
5.41	9.97×10^{-10}
3.64	5.00×10^{-10}
0.20	1.25×10^{-10}

Source: BSC 2003o, Table 7. DTN: MO0002EBSDDC02.003.

No other specific tests have been performed simulating the configuration of the invert; however, tests on the invert material, iron and tuff, have been performed. The results of these tests, as discussed in Section 3.3, are used. For example, for the radionuclide partitioning, the same distribution coefficients tabulated in Table 3-2 are applied.

4.3 MODEL FOR COLLOID-FACILITATED TRANSPORT IN INVERT

This section summarizes the algorithm used to reevaluate the colloid stability. The logic implemented in the TSPA-LA model is provided, although specific programming details are not.

4.3.1 Two Flow Regimes in Invert

The crushed tuff in the invert in the current LA design is characterized by intergranular pore space (pore space in between the aggregate) and intragranular pore space (pore space in the matrix aggregate) (BSC 2003j; BSC 2003k; BSC 2003o). The intragranular pore space has a relatively low intrinsic permeability and porosity whereas the intergranular pore space has a relatively high permeability and porosity. After the thermal period the invert should achieve hydrologic equilibrium with the host rock through capillary action or imbibition, that is, water saturations in the intragranular pore space will reach approximately 90 percent (same as host rock matrix) and water saturations in the intergranular pore space will remain near zero. During the thermal period the pore space in the invert will be dry or near dry and water will gradually enter the intragranular pore space as the invert cools.

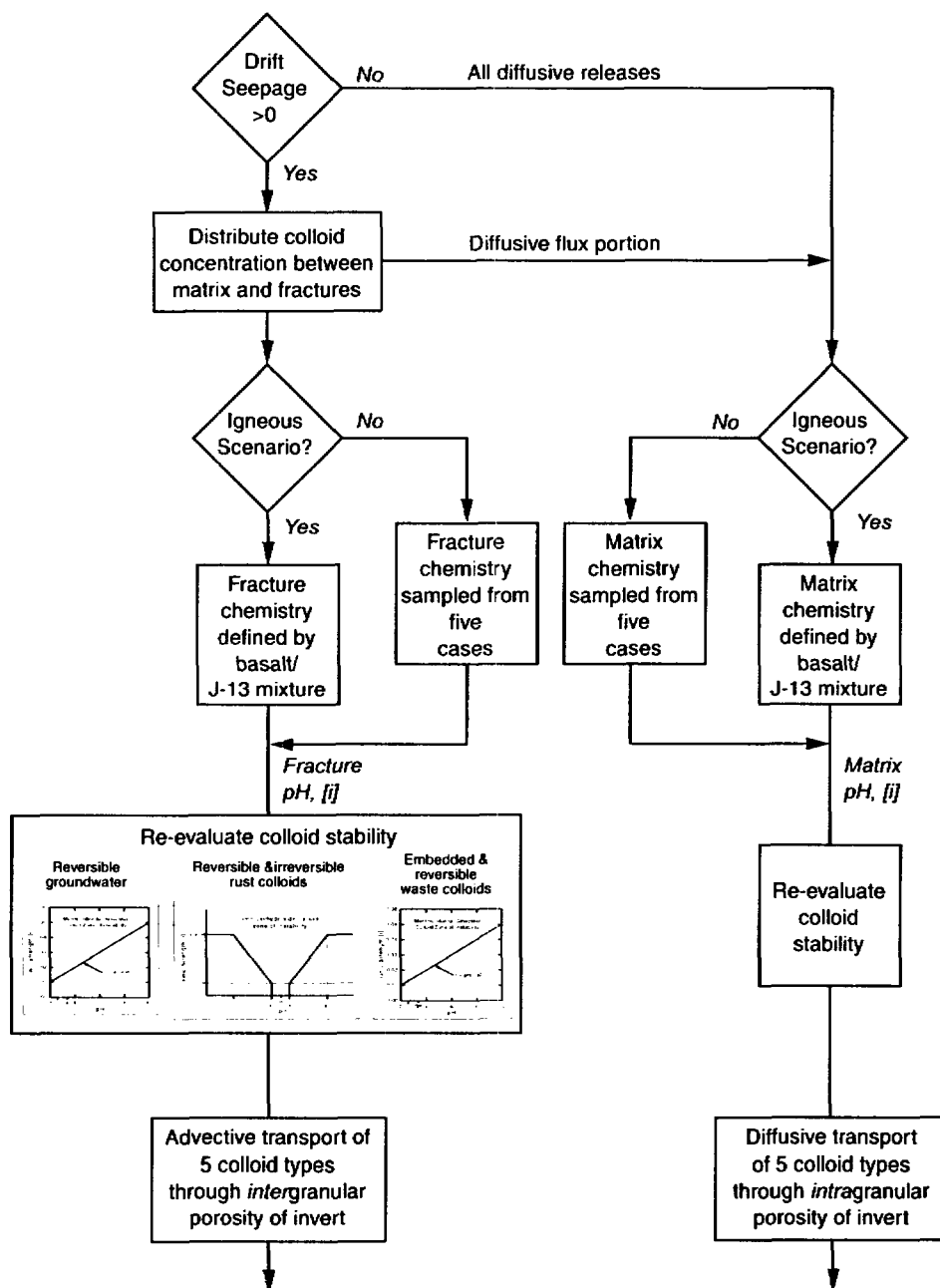
4.3.2 Algorithm Overview

The algorithm for the invert cell (BSC 2003k) divides the invert into these two pore spaces and implements the chemistry that corresponds to each pore space. That is, first, waste-package releases are partitioned into two fractions (Figure 4-2): (1) the intergranular pore space release fraction and (2) the intragranular pore space fraction. An important simplification is made by assuming no mass transfer occurs between the two pore spaces. The partition of the flow in the two flow regimes in the algorithm differs for the three main scenarios evaluated: nominal scenario, seismic scenario, and igneous scenario. The flow fraction entering the intragranular pore space is transported by diffusion using chemistry (i.e., ionic strength and pH) appropriate for the tuff matrix, as evaluated by the drift-scale thermal-hydrologic-chemical model (BSC 2003p) and then evolved by the physical and chemical environment model (BSC 2003k). The flow fraction entering the intergranular pore space is transported by advection and diffusion using chemistry appropriate for the fractures using the tables developed by the physical and chemical environmental model (BSC 2003k).

Second, the abstraction determines the stability of the colloidal mass as a function of ionic strength and pH, using the same stability curves as developed for the colloidal source-term discussed in Section 3. Third, the amount of radioisotopes reversibly sorbed on colloids is recalculated based on the radioisotope solubility for cesium, americium, plutonium, protactinium, and thorium adjusted for the appropriate invert chemistry. Finally, the colloids are transported via diffusion or advection through the invert.

4.3.3 Partition of Contaminated Water Between Inter- and Intraporosity of Invert

The distribution of water contaminated with dissolved radioisotopes and colloids with radioisotopes attached to the inter- and intraporosity of the invert depends on whether the nominal, seismic, or igneous scenario is being evaluated. In turn, the appropriate water chemistry to evaluate the stability of colloids is dependent upon whether the colloids enter the inter- or intraporosity of the invert.



Source: BSC 2003k.

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Figure 4-2. Colloidal Transport Algorithm within the Invert

4.3.3.1 Nominal Scenario

The nominal scenario represents the collection of FEPs most likely to occur. Based on corrosion analysis, the drip shield will remain intact for the regulatory period and, thus, any seepage water that enters the drifts will be diverted away from the waste package. Hence, the only source of water is condensation or dripping of condensation onto the waste package. With this limited amount of water, in the nominal scenario the waste packages do not fail through generalized or localized corrosion or stress corrosion cracking within the 10,000-year regulatory period. This is

similar to the model treatment in the TSPA for the site recommendation (DOE 2002). Hence, for the nominal scenario, releases can only occur because a small fraction of the waste packages have small manufacturing defects. In this situation, all the releases occur via diffusive pathways through the manufacturing defects in the waste packages. Within the shadow of the drip shield, most radionuclides will be transported via diffusion through the intragranular pore space. Diffusive transport through the intergranular pore space will be insignificant since water saturations in the upper portion of the invert will be near zero. Diffusive transport of colloidal material through the intragranular pore space of the invert will likely be small, since the diffusion coefficient for colloids is at least 100 times smaller than for dissolved species based on the relative size of colloids to dissolved species. The colloidal diffusion coefficient can be estimated from the following Stokes-Einstein relationship (BSC 2003o).

$$D_{coll} = D_{ion} \left(\frac{r_{ion}}{r_{coll}} \right) \quad (\text{Eq. 4-1})$$

where D_{coll} is the diffusion coefficient for a colloidal particle of radius r_{coll} and D_{ion} is the diffusion coefficient of an ion of radius r_{ion} . Given a typical ion radius and colloidal particle radius of 0.1 and 1 nm, respectively, the diffusion coefficient of a colloidal particle is generally 100 times smaller than that of a dissolved ion.

Furthermore, the characteristic time (T) for dissolved radionuclides to diffuse through the invert of thickness L can be calculated by:

$$T = L^2 / D \quad (\text{Eq. 4-2})$$

where D is the diffusion coefficient. For an invert transport thickness of 0.8 m, the characteristic time T for colloid diffusion is ~3000 years at 90 percent saturation (i.e., the diffusion coefficient is $6.09 \times 10^{-8} \text{ cm}^2/\text{s}$ for colloids for 90 percent saturation, which corresponds to a moisture content of 49 percent in Table 4-1, assuming porosity equal to 0.54 for the tuff).

Any mixing that occurs between waters in the shadow of the drip shield will be by the slow process of diffusion of anions and cations. The water chemistry in this shadow will remain similar to matrix pore water as ions migrate and react with the water constituents and minerals in the matrix. Thus, the chemistry for evaluating the stability of the colloids corresponds to the matrix pore water chemistry as determined by the physical and chemical environment model (BSC 2003k).

4.3.3.2 Seismic Scenario

In the seismic scenario evaluated out to 10,000 years, an earthquake damages both the drip shield and the waste package. Hence, some advective transport of colloids can occur for those fractions of packages that encounter dripping water. Colloidal releases from diffusion for those packages that either do not have damaged drip shields or do not encounter dripping water will likely be negligible as described for the nominal scenario. In those packages encountering dripping water, colloidal releases can also occur through diffusion into the inter- and intragranular porosity of the invert. Unlike the nominal scenario, intergranular diffusion could occur since the invert saturation will not be zero for waste packages with dripping water. Consequently, the stability of

colloids that are advected through the invert or diffuse via the intergranular porosity must be evaluated using the fracture water chemistry as estimated by the physical and chemical environment model (BSC 2003k).

4.3.3.3 Igneous Scenario

In the igneous scenario, an igneous dike is envisioned to intersect the repository. Two distinct zones are formed. In Zone 1 where the disposal drifts are intersected by the dike, the drip shields and packages are assumed to be disrupted and breached from either the shock wave or heat from the igneous intrusion. In Zone 2, no damage is assumed to occur, and, thus, the same conditions used in the nominal scenario are assumed. Degradation of the waste and formation of colloids in both Zones 1 and 2 is assumed to occur once the drift cools. In Zone 1, the drift is assumed to be completely filled and the host rock and waste package disrupted enough that the drift no longer influences water percolating through Yucca Mountain. Hence, a uniform percolation flux through drifts and waste is hypothesized. Consequently, advective transport of colloids from all the packages through the invert will occur in Zone 1. The water chemistry for evaluating the stability of the colloids is modeled as that formed from the pore water equilibrated with basalt.

4.3.4 Re-evaluation of Colloidal Stability and Solubility

Based on the appropriate ionic strength and pH of the seeping water carrying the colloids in the invert, the colloid stability is reevaluated. Because the material is the same, the stability functions developed and used for the source-term (Section 3) are used in the invert as well. Irreversibly attached plutonium and americium are modeled as a separate dissolved species. If the water chemistry is such that the colloids are unstable, colloids would flocculate and settle out. This situation is modeled as if the “species” precipitated. If at a later time step, the water chemistry is such that the colloids are stable, then the irreversibly attached and embedded colloids are assumed to be resuspended and modeled as if the species redissolved.

The situation is different for colloids with reversibly attached radioisotopes. If the colloids are unstable, then they would flocculate and settle out. However, the radioisotopes are still assumed to be reversibly attached and able to desorb if the solution is below the solubility limit. Then, the solubility of the radioisotopes is reevaluated based on the invert water chemistry.

4.3.5 Re-evaluation of Adsorption

In the final step, the dissolved radioisotope mass is redistributed between the solution and total number of colloids that are available based on the colloid stability functions and the reversible adsorption coefficients (K_{ds}). The total number of colloids is used since the conceptual model does not exclude iron oxyhydroxide (rust) colloids with irreversible attached radioisotopes from also reversibly adsorbing radioisotopes.

A distinct difference, however, is that irreversible adsorption on iron rust colloids is no longer active in the invert. Adsorption on immobile tuff material can occur in the invert, but is probably only minor. The adsorption coefficients for tuff are small (three orders of magnitude less than iron rust) and so adsorption on the 0.8 m maximum thickness of the invert will be small compared to potential adsorption in about 300 m of unsaturated tuff. Steel support structures will be placed throughout the invert to support the steel rails on which the waste packages and

drip shields will be transported, and on which the emplacement pallets will be placed. When this support corrodes, much of the iron rust will remain in the invert. In addition, communication and electrical cables will eventually corrode, leaving copper oxides in the invert. Although these oxides are capable of sorbing substantial amounts of radioisotopes, the oxides will be highly localized and widely separated in relation to the 5-m-long waste packages. For example, the transverse support beams in the invert are spaced 1.5 m apart (BSC 2003o). Thus, the oxides will reside in a strip several centimeters wide separated by 1.5 m of crushed tuff containing little corrosion products. In short, these materials are out of the general flow paths under the waste package, and they are of small spatial extent. Thus, the chance of radioisotopes being released from the waste package and passing through the adsorbing oxides is not great.

4.3.6 Advective and Diffusive Transport

The final step is the evaluation of the advective transport of radioisotopes attached to colloids out of the invert cell based on the fluid velocity through the cell, and the diffusive transport of colloids based on the colloid concentration gradient and the colloid diffusion coefficient (D_{coll}). The colloid diffusion coefficient is set 100 times smaller than the diffusion coefficient of dissolved radioisotopes based on the 100 times difference between the ionic radius of a radioisotope and the radius of a colloidal particle. The actual calculation involves the solution of a similar one-dimensional differential equation used when evaluating transport within the waste package mentioned in Section 3.

Intergranular pore space water saturation during the postclosure period is calculated based on an analysis that defines intergranular pore space saturation as a function of dripping flux. The saturation of the intragranular porosity is assumed equal to the tuff matrix saturation, based on the *Multiscale Thermohydrologic Model* (BSC 2003n).

4.4 UNCERTAINTY AND SENSITIVITY

4.4.1 Uncertainty in Chemical Environment

Within the invert, the stability of colloids and the solubility of radioisotopes is a function of the chemical environment. For the nominal and seismic scenarios, the uncertainty in composition of seepage water entering the emplacement drifts and the invert during the postclosure period is represented by five different seepage water groups. The time-dependent compositions of these five seepage groups are provided by the drift-scale thermal-hydrologic-chemical model (BSC 2003p) and the in-drift physical and chemical environment model (BSC 2003k). Each seepage water group includes two water types, matrix water and fracture water. Fracture water is assumed to enter the emplacement drift by dripping at the crown of the drift. Matrix water enters the drift by imbibition from the host rock matrix into the intragranular pore space occupying the invert ballast material. The capillary pressures in the relatively coarse intergranular pore space are too small to produce imbibition.

When crown seepage drips onto the invert, some of it may imbibe into the intragranular matrix and some of it will flow downward through the intergranular pore space. The dripping water will tend to travel through the intergranular pores since the permeability of the matrix is much lower than the intergranular permeability. Because of the low matrix permeability, advection

through the matrix will be minimal even when seepage is occurring. Water that imbibes into the matrix will react with the matrix water and the minerals in the matrix. Hence, the mixed water in the matrix over time will tend to become similar to matrix water.

The time-dependent fracture and matrix water compositions for each of the five different seepage water groups are used as input to the physical and chemical environment model. The physical and chemical environment model evaporates these different waters over a range of representative environment conditions for the engineered barrier system (e.g., temperature, partial pressure of CO₂, and relative humidity) and the results for both water types—matrix water and fracture water—are abstracted into the form of lookup tables for use by the TSPA-LA model. Each realization selects a water and the corresponding lookup tables for invert and crown seepage chemistry are accessed. The five uncertain water groups are given equal probability weighting.

4.4.2 Uncertainty in Adsorption

The reversible coefficients for adsorption on colloids in the invert are the same coefficients as used in the waste package. Hence, the uncertainty discussed in Section 3.5 is applicable here as well.

4.5 SUMMARY

The distribution of water contaminated with colloids with radioisotopes attached to the inter- and intraporosity of the invert depends on whether the nominal, seismic, or igneous scenario is being evaluated. For the nominal scenario, only diffusive releases can occur and thus the potential for colloidal transport is negligible. For the seismic and igneous scenarios, some advective transport can occur. In these scenarios, the appropriate water chemistry to evaluate the stability of colloids is dependent upon whether the colloids enter the inter- or intraporosity of the invert. Based on the appropriate ionic strength and pH of the seeping water carrying the colloids in the invert, the colloid stability is reevaluated. Because the material is the same, the stability functions developed and used for the source-term (Section 3) are used in the invert as well. In the final step, the dissolved radioisotope mass is redistributed between the solution and total number of colloids that are available, based on the colloid stability functions, and the reversible adsorption coefficients (K_{ds}). Irreversible adsorption on iron rust colloids is no longer active in the invert.

5. TRANSPORT OF COLLOIDS IN UNSATURATED ZONE

This section of the report summarizes the current state of knowledge concerning the transport of radionuclide-carrying colloids in the unsaturated zone, and their release into the saturated zone. The unsaturated zone is the third of the repository system subfeatures examined to determine the importance of colloid transport with respect to the postclosure performance of the Yucca Mountain repository, as shown in Figure 1-1. Modeling assumptions to be used in the TSPA-LA are discussed below.

The information presented in this section primarily draws on the discussions contained in the following documented sources:

1. *Radionuclide Transport Models Under Ambient Conditions* (BSC 2003m).
2. *Unsaturated Zone Colloid Transport Model* (CRWMS M&O 2000d), which is used for reference only in the discussion of the alternate conceptual model of colloid transport, Section 5.5.

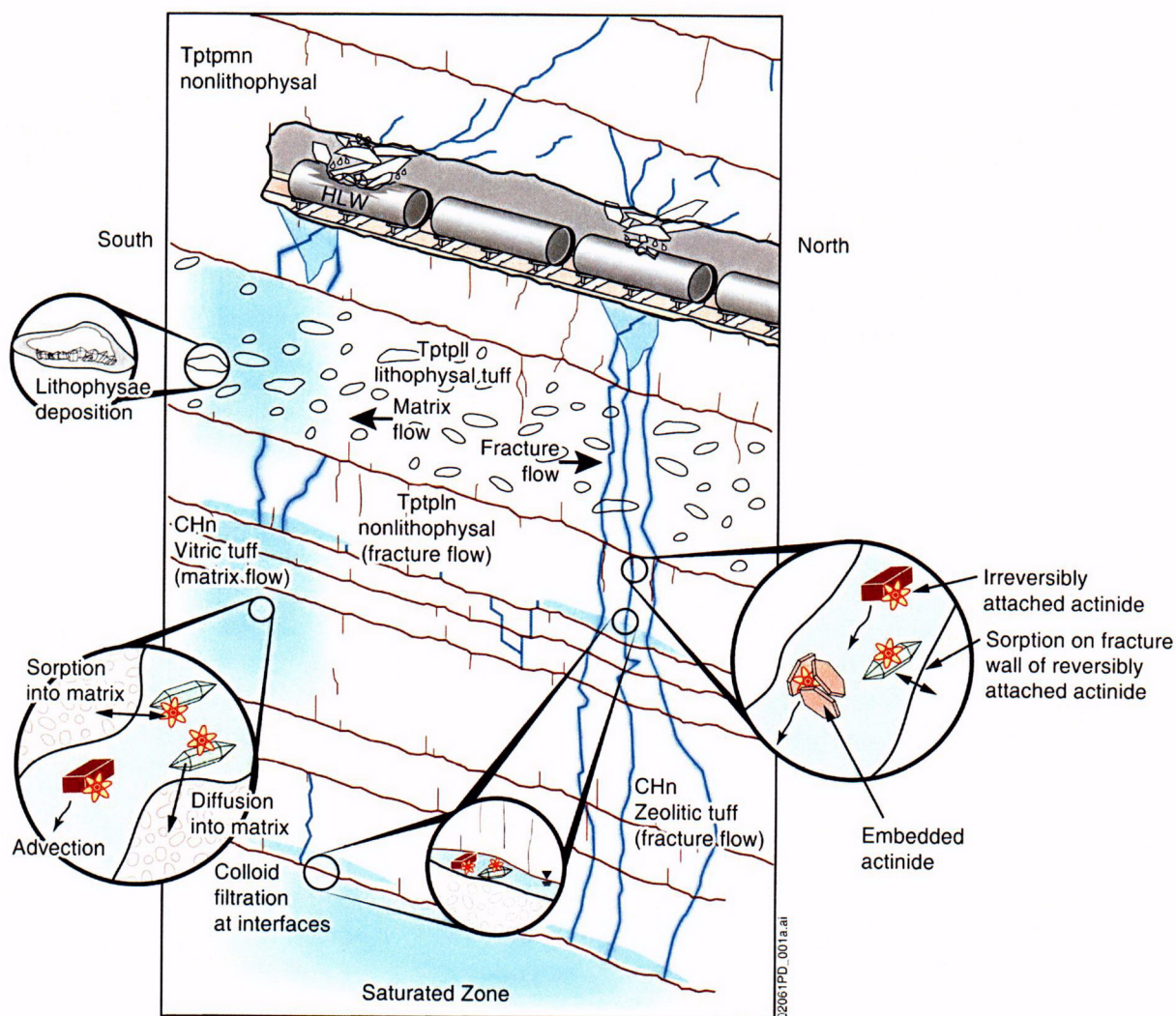
This chapter is organized in the following way: (1) Section 5.1 describes the processes that could occur during the transport of colloids; (2) Sections 5.2 through 5.6 describes the unsaturated zone process model, which includes a subset of the processes described in Section 5.1 along with input data and results; and (3) Section 5.7 describes the TSPA model abstraction.

5.1 DESCRIPTION OF RELEVANT PROCESSES

This section describes processes relevant to the transport of colloids through the unsaturated zone at Yucca Mountain. The discussion focuses on a realistic view of the transport and does not necessarily reflect the conceptual model or numerical models used to predict the transport of colloids through the unsaturated zone. Often in a model conservative assumptions are made when there is a lack of data to support what is believed to be more realistic. Assumptions made in moving to the conceptual model and numerical models used are discussed in Sections 5.2 through 5.6.

Many of the processes relevant to the transport of dissolved species are also relevant to the transport of colloids. However, there are processes unique to colloid transport. Figure 5-1 presents a schematic illustration of colloidal transport processes in the relevant geologic units of the unsaturated zone. Transport below the repository may proceed by two very different means depending on whether devitrified, vitric or zeolitic tuff is encountered. When devitrified or zeolitic rock is encountered, fracture flow will be dominant due to the low permeability of the rock matrix, and colloids will tend to remain in the fractures. When vitric rock is encountered, matrix flow dominates leading to colloid transport mainly through the rock matrix, where colloids are more likely to be filtered or trapped.

The common transport processes are summarized in Section 5.1.1. Transport processes specifically relevant to colloids are summarized in Section 5.1.2. Finally, current information pertaining to colloids at the Yucca Mountain site is summarized in Section 5.1.3.



Transport Processes Relevant to Colloid Transport in the Unsaturated Zone

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Figure 5-1. Schematic Illustration of Colloidal Transport Processes in the Relevant Geologic Units of the Unsaturated Zone

5.1.1 Common Transport Processes

The following transport processes are relevant to both dissolved species and colloids throughout the unsaturated zone.

Advection—Dissolved species and colloids will move by advective transport in groundwater. Advection in fractures is expected to be the dominant transport mechanism in many layers of the various hydrogeologic units. In a few hydrogeologic units, such as the CHv (Calico Hills vitric unit), pp2 (Prow Pass Unit 2), and pp3 (Prow Pass Unit 3) (BSC 2003m, Section 6.6.6), matrix flow is dominant, resulting in much slower transport velocities (compared to those in the fractures of other units) and longer radionuclide-matrix contact times (BSC 2003m, Section 6).

Colloids are much more likely to be filtered in matrix flow than fracture flow because of lower velocities and higher rock surface area to water volume ratios.

Hydrodynamic Dispersion—Hydrodynamic dispersion includes both mechanical dispersion arising from local velocity variations and molecular diffusion driven by concentration gradients. Dispersion of the radionuclides occurs both along (longitudinal) and transverse to the average flow direction. Hydrodynamic dispersion dilutes and smears sharp concentration gradients and reduces the breakthrough time of radionuclides to the water table. The dispersion coefficient is a function of dispersivity and flow velocity.

Hydrodynamic dispersion is not expected to play an important role in unsaturated zone transport. First, significant dispersion effects are implicitly accounted for by the fracture-matrix dual-continuum approach, which explicitly models velocity variations between these continua. Second, the potential repository emplacement area is very broad (relative to the distance to the water table), which tends to make lateral dispersion effects less important (CRWMS M&O 2000e, Section 6.2).

Sorption—Sorption accounts for a combination of chemical interactions between the dissolved radionuclides and the solid phases. The solid phases may be the immobile rock matrix or colloids, which are mobile or immobile depending on their transport characteristics. By removing a portion of the dissolved species from the mobile liquid phase and transferring it to the immobile solid phase, sorption reduces the rate of advance of the concentration front (i.e., retards a dissolved or suspended species). However, the sorption of a dissolved species onto a mobile colloid can enhance the rate of advance of the species relative to its rate of advance as a solute. This process is called colloid-facilitated transport.

Matrix Diffusion—Matrix diffusion plays an important role in radionuclide exchange between the fractures and the rock matrix. Radionuclide diffusion into the rock matrix and away from the fracture surface is driven by a concentration gradient, and it will slow the advance of radionuclides by removing them from the faster flowing fractures. Matrix diffusion of colloids is modeled in the radionuclide transport process model using the Stokes-Einstein equation to represent colloid diffusion rates in water and a tortuosity factor to represent the geometrical effects of the pore structure (BSC 2003m, Section 6.2.6.2).

Radioactive Decay—Radioactive decay reduces the concentration of most radionuclides over time. However, the production of radioactive daughter products adds complexity because transport simulations must compute the total radioactivity distribution (i.e., the sum of the concentrations of all the members of the radioactive decay chain). This is especially significant if the daughters have long half-lives. The daughter products may have significantly different transport behavior than the parent radionuclide. These processes affect both dissolved radionuclides and those attached to colloids.

5.1.2 Transport Processes Relevant to Colloids

The following processes are relevant to colloid transport in the unsaturated zone.

Colloid Deposition onto Rock Surfaces—Colloid deposition (physico-chemical filtration) during flow through a porous medium is commonly assumed to occur in two steps: (1) transport of

colloids to matrix surfaces by Brownian diffusion, interception, or gravitational sedimentation and (2) attachment of colloids to matrix surfaces. The attachment efficiency (i.e., the fraction of collisions resulting in attachment) is strongly influenced by short-range interactions between colloids and matrix surfaces, such as van der Waals and electric double-layer interactions, steric stabilization, and hydrodynamic forces (Kretzschmar et al. 1995, p. 435). The magnitude of these interactions is dependent on water chemistry, colloid and substrate composition and surface chemistry, and water flow rates. Kretzschmar et al. (1997, p. 1,129) demonstrated that colloid deposition generally follows a first-order kinetic rate law and experimentally determined the corresponding collision efficiencies.

Colloid Interactions with Rock and Radionuclides—Colloid attachment to the host rock is strongly dependent on electrostatic interactions. Once attached, colloid detachment (declogging) is generally slow to irreversible. Sorption of radionuclides on colloids is controlled by a number of chemical processes such as ion exchange, surface complexation, and organic complexation (EPRI 1999, p. 4-9).

Colloid Filtration—Wan and Tokunaga (1997, p. 2,413) distinguish two types of straining: conventional straining (if the colloid is larger than the pore throat diameter or the fracture aperture) and film straining (if the colloid is larger than the thickness of the adsorbed water film coating the grains of the rock). Wan and Tokunaga (1997, pp. 2,413 and 2,419) developed a conceptual model to describe colloid transport in unsaturated media as a function of water saturation, S_w . If the rock S_w exceeds a critical saturation value, S_c , colloids move through the system within locally saturated pore spaces. For $S_w < S_c$, colloids can only move in the thin film of water that lines the grain boundaries. Colloid transport through the water film depends on two parameters: the ratio of the colloid size to the film thickness, and the flow velocity. Air–water interfaces are assumed to be immobile and thus impart drag on the colloids as they move through the flowing water in the films. When the film thickness is small enough that the colloids come in contact with both the air–water interface and rock surfaces, the drag forces and surface interactions at both interfaces immobilize the colloid. Temporal variations in the S_w in the subsurface profile and in the infiltration rate can lead to strongly nonlinear colloid mobility in the vicinity of S_c .

McGraw and Kaplan (1997, p. 5.2) investigated the effect of colloid size (from 52 to 1,900 nm) and S_w (from 6 percent to 100 percent) on colloid transport through unsaturated media in Hanford sediments. They showed a very strong dependence of filtration on the colloid size under unsaturated conditions. At a volumetric water content of 6 percent, colloid removal increased exponentially with colloid size. The decrease in colloid mobility at low volumetric water contents was attributed to resistance due to friction (as the colloids were dragged along the sand grains), which is essentially proposed as an alternative or additional film-straining mechanism. Colloid retardation increased as the ratio of the water film thickness to the colloid diameter decreased.

Colloid Deposition onto Air–Water Interfaces—Under unsaturated conditions, colloid transport may be either inhibited or enhanced (relative to saturated conditions) because of the presence of the air–water interface. Wan and Wilson (1994, pp. 857, 863) determined that retention of both hydrophilic and hydrophobic colloids increased with the gas content of the porous medium. They showed that colloids preferentially concentrate in the gas–water interface rather than on the

matrix surface. This tendency increases with the colloid surface hydrophobicity or contact angle, with hydrophobic colloids having the strongest affinity for the gas–water interface. Capillary forces keep the colloids immobilized at the interface. The implications of this colloid behavior may be important. Colloid affinity for the gas–water interface may retard their transport through the unsaturated zone if the interface is not moving. Conversely, if the subsurface conditions permit films to flow, as well as the stability and migration of bubbles, colloid transport may be enhanced. Deposition onto air–water interfaces is differentiated from film straining in that the former occurs when colloids are small relative to water film thickness, whereas the latter occurs only if colloids are large relative to film thickness. In a *deposition* situation, the air–water interface is essentially considered an additional surface to which colloids can attach in an otherwise saturated flow domain. Models of unsaturated colloid transport contain terms that account for film straining, attachment to air–water interfaces, and attachment to rock–water interfaces.

The affinity of colloids for the air–water interface depends on their hydrophobicity and electrostatic charge. Hydrophilic colloids (such as organic colloids and microbes) have a low affinity for the interface, in contrast to hydrophobic colloids (such as mineral fragments). This affinity increases with the positive charge on the colloids (EPRI 1999, p. 6-11). The flow and saturation conditions in the unsaturated zone will determine whether this will enhance or retard transport.

Colloid Detachment from Surfaces/Interfaces—Colloids that are deposited onto surfaces can later become detached and reenter the mobile phase. Detachment can occur as result of random fluctuations in short-range forces between the colloid and rock surface or between the colloid and air–water interface that cause the colloid to “jump” over an energy barrier that normally keeps it immobilized. Alternatively, detachment can be caused by mobile colloids or particles colliding with immobile colloids or by macro-scale transients in flow conditions (saturation or flow rates) and water chemistry, or even by large-scale energy inputs such as seismic events. Detachment is often described as a first-order kinetic process, although many studies have demonstrated that it may be an inherently nonlinear process (Dabros and Van de Ven 1982; Dabros and Van de Ven 1983). If colloid attachment and detachment are both linear first-order processes with rate constants given by k_{att} and k_{det} , respectively, then a colloid retardation factor can be defined as $R_{col} = 1 + k_{att}/k_{det}$.

Colloid Generation in the Unsaturated Zone—Colloids can be generated in the unsaturated zone by several different processes. These include weathering, diagenesis, erosion, and dissolution of material that holds small particles in place on rock surfaces. Episodic flow may generate colloids by sweeping air–water interfaces, which colloids can attach to, across rock surfaces. Generation is important because it increases the mobile surface area for solution-phase radionuclides to adsorb to, and it can also mobilize radionuclides that are adsorbed to surfaces that become transformed into colloids.

Gravitational Settling—Because of their large size relative to solutes and their density contrast with ground water, colloids are subject to gravitational settling. Settling can affect the transport of colloids by enhancing colloid velocities in vertically-oriented fractures and increasing collision frequencies with rock surfaces in nonvertically oriented fractures. Settling velocities

are proportional to the difference in density between colloids and ground water and to colloid diameter squared, so settling is clearly more important for larger colloids.

Film Straining—Film straining occurs when colloids have a greater diameter than the water film thickness. The colloids get sandwiched between the air–water interface and the rock surface, which cause the colloids to become immobilized.

5.1.3 Colloids at the Yucca Mountain Site

Colloids can be categorized as waste-form colloids, corrosion produced colloids, and natural colloids. Waste-form colloids include glass (smectite) colloids with embedded plutonium and americium. For these colloids, the radionuclides are irreversibly attached onto the colloids. These radionuclides transport identically to the transport of the colloid onto which they are attached. Corrosion colloids include iron oxyhydroxide. Dissolved radionuclides may become attached to these colloids either reversibly or irreversibly. Natural colloids include clays, bio-organisms, and smectite. A natural colloid becomes a pseudocolloid when a dissolved radionuclide adsorbs onto it. True (intrinsic) Pu(IV) colloids (generated from the contaminant when its concentration exceeds its solubility) have been produced by the agglomeration of hydrolyzed Pu(IV) ions under acidic conditions (EPRI 1999, p. 3-2).

The available data on colloid occurrence and concentrations at the Yucca Mountain site pertain to saturated zone studies. The current state of understanding is that (1) the natural colloid concentrations in ground water at the Yucca Mountain site are low (106 to 1,010 colloids/mL) and (2) waste-form colloids will be the dominant colloidal species of concern to transport studies (BSC 2003m, Section 6.18.1).

Colloids diffuse more slowly than dissolved species because of their larger size (BSC 2003m, Section 6.2.5, Equation 6-23). For the largest colloids, diffusion is approximately three orders of magnitude slower than that for molecular species (Nuttall et al. 1991, p. 189). For example, the diffusion coefficient, D_0 , of a 0.1 μm colloid (probably not the largest size) at 20°C is $4.29 \times 10^{-12} \text{ m}^2/\text{sec}$ (BSC 2003m, Equation 6-23), while the D_0 of Br is $2.08 \times 10^{-9} \text{ m}^2/\text{sec}$ (Cussler 1984, p.147).

Using mercury porosimetry, Roberts and Lin (1997, pp. 577 to 578) determined that the average pore diameters of welded and densely welded TSw tuff samples were 53.1 nm and 19.7 to 21.4 nm, respectively. These extremely small pores are certain to exclude a significant proportion of colloids. It is possible for colloids to accumulate on the fracture walls and thus clog the matrix pores open to the fracture. This can lead to a reduction in the matrix permeability and a reduction in the colloid diffusion into the matrix.

5.2 MODELING ASSUMPTIONS

The current model for describing transport of dissolved and colloidal species in the unsaturated zone of Yucca Mountain is the unsaturated zone radionuclide transport model (BSC 2003m, Section 6). Only assumptions impacting colloid transport in the unsaturated zone are presented here. The complete list of assumptions for the radionuclide transport model and the discussion of the supporting rationale are in *Radionuclide Transport Models Under Ambient Conditions* (BSC 2003m, Section 6.1.5).

The following assumptions have been made:

1. The individual and combined effects of diffusion (molecular and/or colloidal), surface diffusion, and hydrodynamic dispersion follow a Fickian model. Given the macroscopic continuum approach, this is a valid assumption (de Marsily 1986, pp. 228 through 277).
2. Transport is assumed to occur isothermally at 25°C. This assumption of isothermal transport at the average ambient temperature of the unsaturated zone is consistent with the assumption of isothermal flow at the same temperature. The transport parameters affected by temperature are (1) the diffusion coefficient D_0 of the dissolved or colloidal species and (2) the sorption parameters of the dissolved species or the filtration parameters of the suspended colloid.

Natural temperature differentials in the undisturbed unsaturated zone profile occur because of the geothermal gradient. Substantial temperature increases over the ambient temperature are expected after radioactive waste emplacement in the repository (BSC 2003p, Section 6). An increasing temperature leads to a higher D_0 value (BSC 2003m, Section 6.1.2.9). Based on this relationship, an increase in temperature from 20°C at the top of the unsaturated zone domain to 30°C at the water table leads to an increase of D_0 by about 30 percent.

The effect of temperature on sorption and/or filtration is less well defined. The general effect of an increasing temperature is a decrease in the sorption of anionic species and an increase in the sorption of cationic species. Theoretical and experimental studies indicate an increase of the distribution coefficient K_d with temperature when sorption follows a linear equilibrium isotherm (BSC 2003p, Section 6).

Colloid filtration (deposition) generally follows a kinetic process (BSC 2003m, Sections 6.2.3 and 6.16.2). An increase in temperature increases the forward filtration coefficient, \hat{e}^+ , indicating an increase in the filtration (deposition, clogging) rate (BSC 2003m, Equation 6-31). There is no information on the effect of temperature on the reverse filtration coefficient, \hat{e}^- . Thus, an increasing temperature in the unsaturated zone enhances diffusion and increases sorption and/or filtration. This is a particularly important mechanism in species mass transfer from the flow-dominating fractures to the matrix. The cumulative effect is slower transport.

The assumption of isothermal transport should not be viewed as an approximation of the prevailing conditions in the unsaturated zone, but rather as a condition that reflects a transport scenario that leads to conservative estimates of radionuclide travel times to the water table.

3. The concentration of the radioactive solutes or colloids is too low to have any measurable effect on the flow regime. Colloids and radionuclides migrating from the repository are expected to occur at concentrations that are too low to affect the aqueous solution density (BSC 2003p, Section 6).

4. Filtration of colloids is assumed not to affect the medium porosity and permeability. Waste-form colloids and natural colloids under natural conditions are present in sufficiently small concentrations (BSC 2003m, Section 6.1.5.2) to make this a valid assumption. This reference also indicates that, as a result of conditions adverse to colloid stability (e.g., pH, ionic strength) in the immediate vicinity of the repository, radionuclides in colloidal form will be released in low concentrations for a long time.
5. The dual-permeability model is a valid approximation for flow and transport simulations because it describes the matrix and fractures as separate but interconnected gridblocks and permits flow and transport between matrix gridblocks, fracture gridblocks, and fractures and matrix. A more detailed discussion on the rationale for this assumption can be found in (BSC 2003q, Section 6.1.5.3).

A number of other conservative assumptions are made in the modeling of the transport of colloids through the unsaturated zone. These assumptions are justified as being conservative because their impact would be an overestimation of releases and dose. These are:

6. The conditions for the creation and stability of solute and colloidal species exist, the radioactive tracers (solutes or colloids) are stable, unaffected by the near field conditions (thermal, geochemical, physical). This is a conservative assumption because the elevated temperature and high ionic strength expected in the near field will tend to destabilize colloid suspensions. However, the impact of this conservatism has not been evaluated.
7. The radioactive tracers (solutes or colloids) are not subject to chemical immobilization (e.g., through irreversible sorption or precipitation) anywhere in the unsaturated zone. The impact of this conservatism has not been evaluated.
8. The vertical fractures are assumed to be open and continuous throughout the unsaturated zone from the repository to the water table. This may not necessarily be important based on the results of a study that compared the impact of releasing radionuclides from the repository directly into faults and not releasing the radionuclides into the faults (BSC 2003m, Section 6.20). The analysis shows little difference in colloid concentration histories at the water table. The results indicate that faults are well connected and that colloids are able to make their way to these fast paths when they are released some distance away from the faults.
9. The horizontal fractures are assumed to be interconnected and are also connected (directly or indirectly) to the vertical fractures. While this is a conservative assumption, its impact may not be significant for the reasons stated in the previous assumption.
10. Sorption of colloids on fracture walls or in fractures is excluded. This may be a very conservative assumption. The C-Well tests indicated that retardation of colloids in fractures is significant (see Section 6.4.2 of this technical basis document). Applying the C-Well data from saturated-zone volcanics to the unsaturated zone is conservative (see Section 5.7.2). Additionally, comparisons of results from the radionuclide

transport model with the alternate conceptual model using FEHM (see Section 5.6.3), which considers colloid retardation in the fractures, indicate that colloid retardation in the fractures can significantly delay colloid breakthrough.

11. Film straining of colloids is excluded. This is a conservative assumption as colloids will not become immobilized by this process. The impact of this conservative assumption has not been evaluated.

A summary of the processes in the process-level model for unsaturated zone colloid transport is given below:

1. Advection
2. Dispersion
3. Matrix diffusion
4. Colloid attachment and detachment in the matrix
5. Colloid attachment and detachment in the fracture (assumed to be zero except for sensitivity cases)
6. Pore size exclusion

5.3 SOURCES OF DATA AND TESTING

5.3.1 Data

Only colloid-related data are summarized here. Details concerning other transport processes that may affect colloid-assisted radionuclide transport such as (1) infiltration rate, (2) dispersion, (3) sorption coefficients, (4) matrix diffusion, (5) fracture characteristics, (6) radionuclide decay, and (7) daughter product contributions are described in the specific input data sets and their associated data tracking numbers (DTNs) and sources listed in Table 4-1 of *Radionuclide Transport Models Under Ambient Conditions* (BSC 2003m).

Colloidal Forms and Properties—Four colloids of different sizes were considered (ranging from 6 to 450 nm). Their sizes and their accessibility factors are shown in Table 6.18-1 of *Radionuclide Transport Models Under Ambient Conditions* (BSC 2003m).

Colloid Filtration Model and Coefficients—Pore-size exclusion (straining and filtration) was calculated using the colloid and formation-specific accessibility factors. The clogging (forward) kinetic coefficient $\hat{\epsilon}^+$ is computed using the formulations documented in Section 6.18.2 of *Radionuclide Transport Models Under Ambient Conditions* (BSC 2003m). No information exists on the kinetic declogging (reverse) coefficient $\hat{\epsilon}^-$. Sensitivity results presented in Section 5.4.3 of this report indicate that this is not a significant factor.

5.3.2 Testing

Very limited field-testing or data exists at YMP or in the open literature concerning the transport of colloids through unsaturated media. The Busted Butte field test in nearby unsaturated rock was conducted in part to provide data, confirmatory evidence, and a validation basis for the transport of colloids through the unsaturated zone at Yucca Mountain. Additional details for the Busted Butte tests can be found in *Unsaturated Zone and Saturated Zone Transport Properties* (CRWMS M&O 2001b).

The Busted Butte test facility is located in Area 25 of the Nevada Test Site approximately 160 km northwest of Las Vegas, Nevada, and 8 km southeast of the potential Yucca Mountain repository area. The site was chosen based on the presence of a readily accessible exposure of the Topopah Spring Tuff and the Calico Hills Formation and the similarity of these units to those beneath the potential repository horizon. The colloids consisted of two sizes of fluorescent polystyrene microspheres of 0.3 and 1.0 μm .

Carboxylate-modified polystyrene latex (CML) microspheres were significantly attenuated in the unsaturated media at Busted Butte. However, the microspheres were typically injected in relatively high-ionic-strength solutions of solute tracers that would have tended to destabilize them and make them more susceptible to attachment to rock surfaces. Also, flow at Busted Butte was matrix dominated, not fracture dominated. For these reasons, the Busted Butte microsphere experiments probably do not provide a very good representation of colloid transport in fractures in the unsaturated zone. No evidence of microsphere breakthrough was observed in either test Phase 1B or Phase 2. Because of this, microspheres were eliminated from the experimental matrix early on in Phase 2.

Because data and field testing of colloid transport in the unsaturated zone is limited and difficult to obtain, the data resulting from the C-Wells, conducted in the saturated zone, could serve as a conservative estimate in that it overestimates transport. These data are not used in the radionuclide transport model, which takes a conservative approach by not considering sorption of colloids in the fractures or on fracture walls. However, the TSPA-LA treatment of colloid transport in the unsaturated zone does consider the use of the C-Wells data to support colloid retardation in unsaturated zone fractures. The application of the C-Wells data from saturated zone volcanic fractures to unsaturated conditions is conservative (see Section 5.7.2, Assumption 6 and discussion in remainder of Section 5.7.2). The saturated zone used the C-Wells field test data (BSC 2003b), which results in considerable retardation of colloids in both the vitric and alluvial regions of the saturated zone (BSC 2003a). The characteristics observed in the C-Wells field test data are summarized below.

Details for the C-Wells tests are documented most thoroughly in *Saturated Zone In-Situ Testing* (BSC 2003d). To estimate retardation of colloids in the fracture continuum, field experiments at the C-Wells complex near Yucca Mountain were examined, in which CML microspheres were used as analogs for colloids (BSC 2003d). Tests were conducted at the C-Wells (UE-25c#1, c#2, and c#3), which are located approximately 2 km southeast of the potential repository footprint, and completed in fractured volcanic tuffs. Microsphere tracer experiments were conducted in both the conductive Bullfrog Tuff and less conductive Prow Pass Tuff. The breakthrough curves

were fitted to obtain estimates of forward and reverse filtration rates. These were then used to calculate a retardation factor for colloid transport through saturated fractured rock (BSC 2003b).

5.4 MODEL OF COLLOID-FACILITATED TRANSPORT IN THE UNSATURATED ZONE

5.4.1 Purpose

The purpose of this modeling is to evaluate the transport of radioactive solutes and colloids in the unsaturated zone under ambient conditions from the repository horizon to the water table at Yucca Mountain.

The unsaturated zone radionuclide transport model (BSC 2003m, Section 6) considers:

1. The transport of radionuclides through fractured tuffs.
2. The effects of changes in the intensity and characteristics of fracturing among different hydrogeologic units.
3. Colloid transport of irreversibly attached radionuclides.
4. Physical and chemical retardation processes.
5. The effects of different conceptual representations of the matrix-fracture system.
6. The effects of different modeling approaches in the characterization of the transport problem.

Radionuclides may interact with colloids in different ways. Sorption/desorption reactions for radionuclides onto colloids may be relatively fast leading to equilibrium between the aqueous and sorbed state. This type of interaction between radionuclides and colloids is termed "reversible". Alternately, the interaction may be a result of fast sorption and relatively slow desorption such that the radionuclide may be considered permanently sorbed onto the colloid. Strong radionuclide-colloid interactions may also be a result of the radionuclide being embedded in the colloid material itself. This type of interaction between radionuclides and colloids is termed irreversible. For radionuclides irreversibly attached to colloids, the transport of the radionuclides and the colloids are equivalent.

Because there are indications that colloid-facilitated transport for radionuclides with reversible interactions with colloids will not be significant, only irreversible colloids were considered in the radionuclide transport model simulations (BSC 2003m, Section 6.18.1). The irreversible colloids were taken to have the properties of PuO_2 and are subject to radioactive decay. Four colloids of different sizes were considered. Note, however that colloid facilitated transport for radionuclides with interactions with colloids are included in the TSPA colloid facilitated radionuclide transport model (see Section 5.7 of this report).

5.4.2 Implementation

Flux Terms—The mass balance equations that are solved in the radionuclide transport model are written in part in terms of species or contaminant flux. In general, the flux term has contributions from advective, diffusive, and dispersive transport processes.

For the situation of evaluating colloid flux the following modifications are required:

1. Surface diffusion does not occur in colloids.
2. The Darcy velocities which are used to determine the dispersion tensor and ultimately the flux term are multiplied by the factor f (greater than 1), to reflect the observations that colloids move at a velocity greater than the average fluid velocity.
3. The longitudinal and transverse dispersivities are generally different from those for solutes (Ibaraki and Sudicky 1995) and may be a function of the colloidal particle size.
4. The term, D_0 , is the colloidal diffusion coefficient in water and is described by the Stokes-Einstein equation, according to Bird et al. (1960, p. 514).
5. The fluxes are multiplied by the colloid accessibility factors f_c at the interface of different media. The f_c factor describes the portion of the colloidal concentration in a medium that is allowed to enter an adjacent medium of different characteristics, and quantifies pore size exclusion (BSC 2003m, Section 6.2.6.2).

Because it is directly proportional to the water fluxes, advection in the fractures is by far the dominant mechanism of transport in the unsaturated zone of Yucca Mountain. Transport is further enhanced by longitudinal dispersion and molecular diffusion. Coupled with the fracture orientation and gravitational differentials, the result of the fracture and flow characteristics is a mainly downward migration of the radionuclides. Note that advection also occurs in the matrix (and is accounted for in the simulations), albeit at significantly lower rates.

Lateral spreading of the contaminants can be achieved through transverse dispersion, and molecular diffusion. As sorption occurs from the liquid phase onto the solids, and fractures are by far the main conduits of water, retardation of sorbing radionuclides will be controlled by sorption of radionuclides onto fracture surfaces and the rate of radionuclide movement from the fractures to the sorbing matrix. This is represented by the sum of diffusive, dispersive, and surface diffusion fluxes, and results in the lateral migration of the contaminants. In the radionuclide transport process model sorption of colloids on fracture surfaces is conservatively not considered.

Colloid Filtration Term—Colloidal filtration is included in the model application using a linear kinetic model by Çorapçıoğlu et al. (1987, pp. 269 to 342).

Filtration is one of the main mechanisms of radioactive colloid removal from the transporting liquid phase, the others being chemical destabilization due to pH and ionic strength changes and flocculation. Three types of filtration mechanisms may affect the transport of colloids through

the permeable fracture/matrix media: surface filtration, straining filtration, and physical-chemical filtration:

1. Surface filtration occurs when particles are larger than the pores, in which case a filter cake is formed; colloids if they are small enough can enter the matrix by advective and diffusive processes.
2. Straining filtration is determined by the ratio $R_d = d_g/d_p$, where d_g is the diameter of the grains of the porous medium and d_p is the suspended particle diameter. Herzig et al. (1970, p. 15) indicated that little straining was expected when R_d is greater than 12, and calculated that when $R_d = 50$, only 0.053 percent of porosity would be occupied by particles.
3. A detailed discussion of the physical-chemical filtration of colloids can be found in Çorapçıoğlu et al. (1987, pp. 269 through 342). The physical-chemical colloidal filtration by the porous/fractured medium involves three mechanisms: (1) contact with the pore walls, (2) colloid fixation onto the walls, and (3) release of previously fixed colloids (Herzig et al. 1970; Çorapçıoğlu et al. 1987). Contact with the pore walls and colloidal capture can be the result of:
 - a. sedimentation (caused by a density differential between the colloidal and the carrier liquid),
 - b. inertia (deviation of colloidal trajectories from the liquid streamlines because of their weight),
 - c. hydrodynamic effects (caused by a variation in the velocity field of the liquid),
 - d. direct interception (caused by collisions with the pore walls at convergent areas), and
 - e. diffusion (Brownian motion causing colloids to move toward pore walls or dead-end pores).
4. Fixation on the pore walls occurs at retention sites that include edges between two convex surfaces, pore throats smaller than the colloidal size, and dead-end pores or regions of near-zero liquid velocity. Fixation is caused by retentive forces, which include axial pressure of the fluid at constriction sites, friction forces, van der Waals forces, electrical forces and chemical forces (Herzig et al. 1970, pp. 4, 11 through 17).
5. Remobilization of colloidal particles may be caused by a number of factors, including collision between a loosely held colloid and a moving particle, an increase in pressure as colloids constrict flow, and a change in the chemical environment.

All three mechanisms are expected to be present in the unsaturated zone. The simulations of the unsaturated zone transport model can account for surface filtration by using a particle size versus pore size criterion, and by not allowing colloidal entry into media that do not meet this criterion. Straining filtration (pore-size exclusion) is described by using appropriate colloid accessibility

factors (BSC 2003m, Section 6.3.5), and physical-chemical filtration is represented by using appropriate kinetic parameters (BSC 2003m, Equations 6-14 or 6-15).

Cake filtration and the effects of filtration on permeability and porosity are unlikely in the unsaturated zone because (1) natural pseudocolloids (such as clays) under natural conditions occur in small concentrations and (2) it is expected that, owing to chemical conditions adverse to colloid stability (e.g., pH, ionic strength) in the immediate vicinity of the repository, colloids will be released at low concentrations for a long time.

Colloid-Assisted Transport Terms—In the radionuclide transport model, colloid assisted transport is considered for radionuclides that are irreversibly sorbed onto colloids. Radionuclides that are both irreversibly and reversibly sorbed onto colloids are considered in the TSPA-LA unsaturated zone transport model, see Section 5.7 of this report.

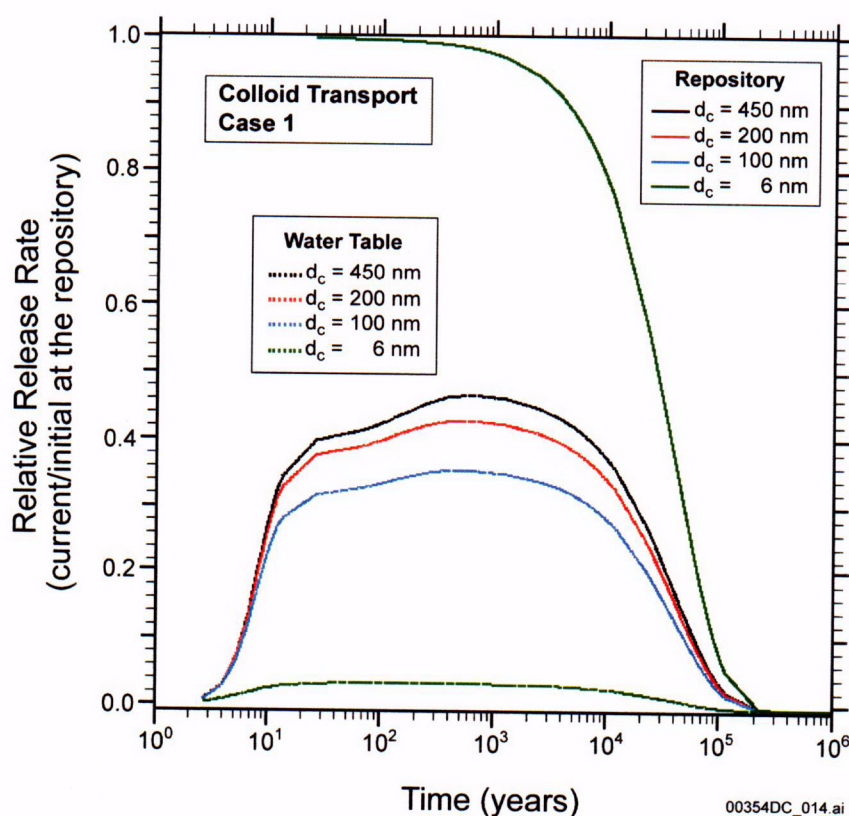
The formulation used allows consideration of the whole size spectrum of a particular colloid, as each size would have different transport behavior and different sorption properties (resulting from different surface area). Of particular interest in unsaturated zone radioactive transport models is the potential of colloid-assisted transport to significantly enhance the migration of radionuclides whose normally strong sorbing behavior would confine them to the vicinity of the release point. Sorption of such a radionuclide (e.g., plutonium) onto pseudocolloids renders the colloid radioactive. The transport of such a radionuclide is no longer dictated by the strong radionuclide sorption behavior, but by the kinetics of colloid filtration. The kinetics of colloid filtration coupled with the fact that colloids can move at velocities up to 50 percent higher than the Darcy velocity, can result in travel times to the water table orders of magnitude shorter than the ones predicted by solute-based transport modeling.

Daughter Products of Radioactive Decay—Radioactive decay and the transport of daughter products is taken into account for both dissolved and colloid related radionuclides.

If decay results in radioactive daughters, unsaturated zone simulations must compute the total radioactivity distribution (i.e., the sum of the concentrations of all the members of the radioactive decay chain). This is particularly important for daughters that have long half-lives. The formulation requires knowledge of the mass fraction of the decayed sorbed parent that remains sorbed as a daughter. This mass fraction is a function of the type of decay, as well as of the chemical form of the sorbed cation. In alpha decay (e.g., ^{237}Np , ^{239}Pu), it is 0. There is no information on the behavior of mass fraction for other types of decay. This mass fraction can have significant implications for the transport behavior of daughters if (1) the large sorbed masses of strongly sorbing parents are ejected back into the aqueous phase after decay, (2) the daughter is a much weaker sorber, and (3) the daughter's sorption is kinetically controlled. Such a possibility could arise in kinetically dependent sorption of radionuclides onto pseudocolloids (CRWMS M&O 2001b, Section 6). For equilibrium isotherms this is not significant.

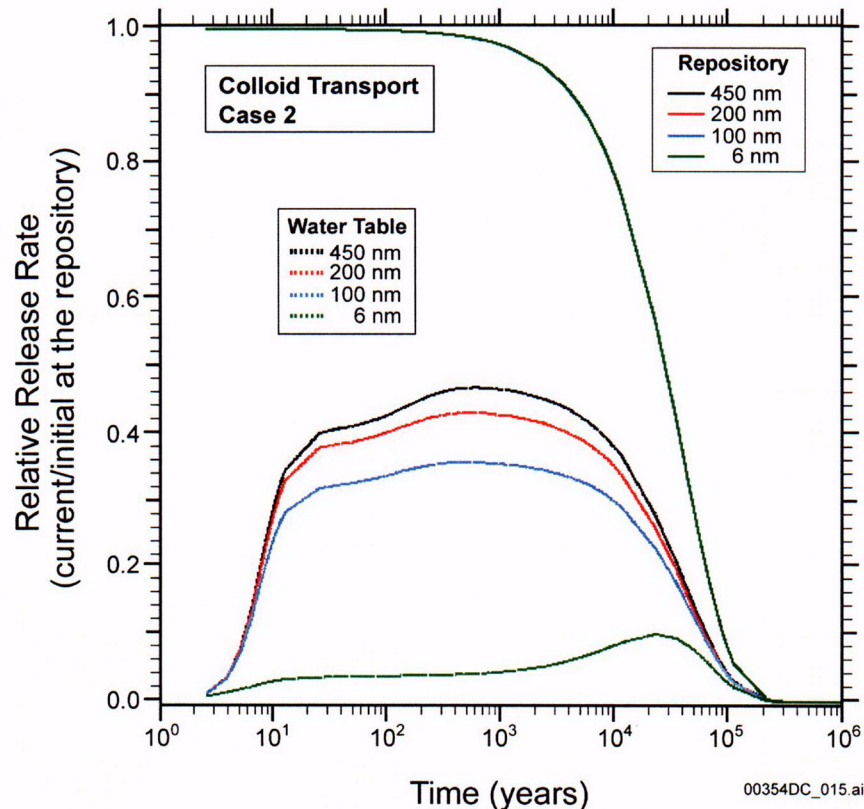
5.4.3 Results

The results from the four colloid transport simulations using TOUGH2 V1.11MEOS9nTV1.0 (Module EOS9nTV1.0) (LBNL 1999a) are discussed in detail in Section 6.18 and Attachment VI of *Radionuclide Transport Models Under Ambient Conditions* (BSC 2003m). Example results from case 1 (no declogging [colloid detachment]) and case 2 (strong declogging) are shown here in Figures 5-2 and 5-3, respectively. Each figure contains two sets of four curves, one for each colloid-size particle. The set labeled “Water Table” indicates the relative release rate at the unsaturated zone-saturated zone interface. The set labeled “Repository” indicates the decaying plutonium colloid source term for each of the colloid particle sizes considered as leaving the repository and entering the unsaturated zone. Note that the four curves labeled “Repository” exactly collapse into a single curve in both figures because the release from the repository is identical for all colloid sizes. The rapid drop in all of the curves is due to radioactive decay.



Source: DTN: LB991220140160.017.

Figure 5-2. Example Results from Case 1 (No Declogging)



Source: DTN: LB991220140160.017.

Figure 5-3. Example Results from Case 2 (Strong Declogging)

Colloid Transport Case 1—This simulation assumes that no declogging (detachment) occurs once colloids are attached to the matrix. Two observations appear particularly important:

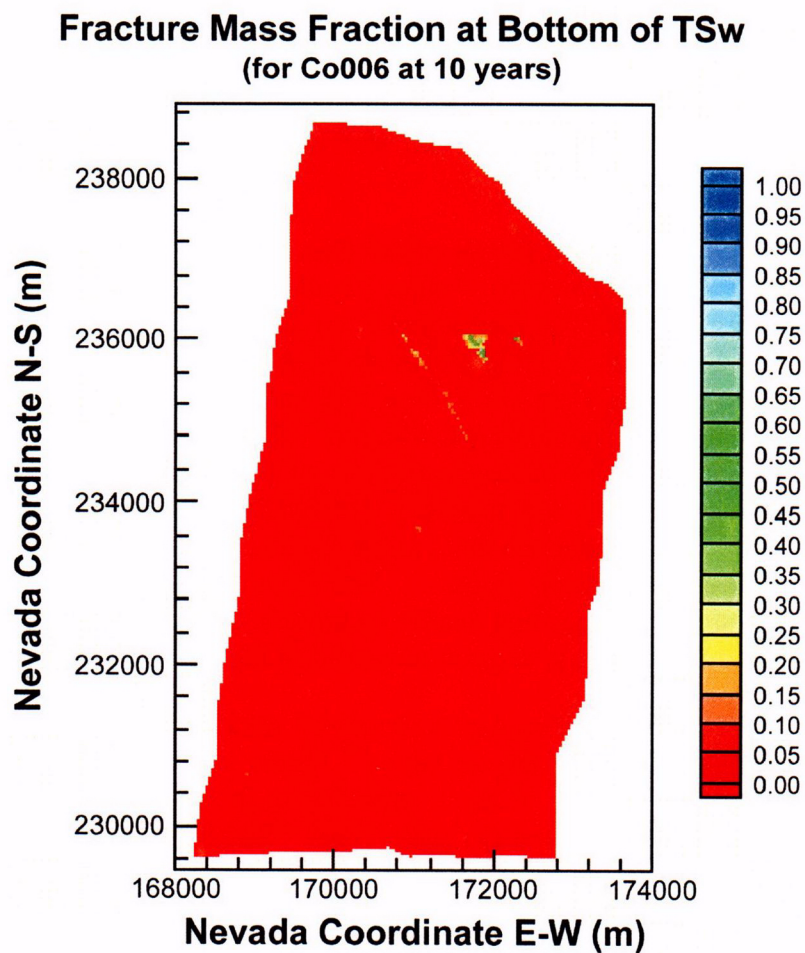
1. The very fast breakthrough of the larger colloids (characterized by a rapid rise of the breakthrough curves), the rapidity of which is about the same for all the larger colloids (greater than or equal to 100 nm).
2. The smallest colloid (6 nm) has the slowest breakthrough. It is really noteworthy that this colloid never reaches the 0.1 fraction level, indicating that it is sufficiently small compared to the larger colloids to enter the matrix and get attached to the fracture walls. This behavior results from a combination of the following factors:
 - a. The larger colloids, because of their size, can only move in the center of pores/fractures where velocities are higher than the average water velocity. However, this will only result in colloids moving at most 1.5 times the average velocity.
 - b. The inability of larger colloids to penetrate into the matrix from the fractures because of size exclusion. Thus, the colloid mass in the fractures is not reduced through colloidal diffusion and/or hydrodynamic dispersion, and since retardation in fractures is excluded, practically all of it moves exclusively in the fractures.

Colloid Transport Case 2—In Case 2 there is a strong declogging factor, while in Case 1 there is no declogging. The differences in breakthrough curves between Case 1 and Case 2 are very small for all colloids, and are most prominent in the case of the 6-nm colloid. The relative insensitivity to the clogging model in the matrix indicates the dominant role of the fractures in the three-dimensional site scale system, with the matrix appearing to have a negligible contribution.

Colloid Transport Mechanisms and Patterns for Case 1—Details of the transport patterns are provided in the *Radionuclide Transport Models Under Ambient Conditions* (BSC 2003m, Section 6.18, Attachment VI and VII). The importance of fractures on the transport of the 6-nm colloid (Co0060) is evident in the results, which show colloid concentration contours after ten years (Figure 5-4). Despite the very early time, the colloid concentration in the fracture is substantial, and it approaches the release concentration. The reasons for the significant presence (in terms of areal extent and level of concentration) of the 6-nm compared to the dissolved colloid are that (1) diffusion into the matrix is limited because of its relatively large size (compared to solutes) and pore exclusion and (2) the tsw39 model layer is above the TSw-CHn interface, where significant filtration occurs. The results also indicate that the colloids accumulate at the TSw-CHn interface and, unable to cross it, move along the sloping interface in an easterly direction. This transport is more pronounced in the 6-nm colloid than in the solutes.

Results of the matrix F_R (relative filtered concentration) distributions at various times indicate more filtration in the northern part of the repository. Figure 5-5 illustrates this at 10,000 years. This is indicated by the large amount of areal spreading in the relative concentration (in green) about the higher fracture concentration (in light blue). Since the dominant pathway for the transport of colloids through the zeolitic rock in the north is through fractures, this spreading is caused by the inability of the colloids to migrate through the interface between the TSw and CHn layers. This is consistent with the permeability barriers that result in the perched water bodies at this location. The matrix-filtered relative concentrations are higher in the south (in dark blue) and this is due to the presence of vitric tuff where the matrix and fractures more equally share in the vertical transport of the 6-nm-size colloid and not due to lateral spreading at the interface. More details of these results and further explanations are presented in Section 6.18 of *Radionuclide Transport Models Under Ambient Conditions* (BSC 2003m).

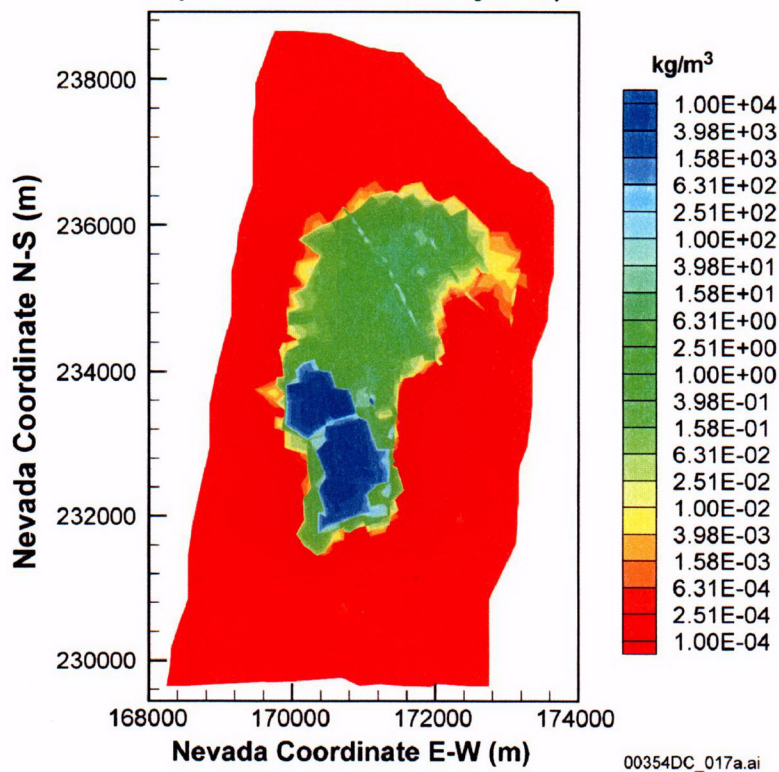
At $t = 1,000$ years (Figure 5-6), the concentration in the fractures exceeds that in the water released from the repository. This is caused by pore-exclusion (straining) at the TSw-CHn interface, which leads to the accumulation of the 6-nm colloid in the tsw39. Results showing mass fraction concentration at the water table at 1,000 years follow patterns analogous to those in the tsw39 layer (Figure 5-7). The fracture X_R (relative mass fraction) above the water table exceeds that in the water released from the repository, and the differences between the two increases with time. This occurs because of the fast transport of the colloids in the fractures and their accumulation. This accumulation is caused by the very significant pore-size exclusion and kinetic (physical-chemical) filtration at the water table, which prevent colloids from entering the saturated zone while allowing water to flow into it. This occurs because the saturated zone behaves as a porous (rather than a fractured) medium with the properties of the TSw matrix.



Source: BSC 2003m, Figure VI.1.

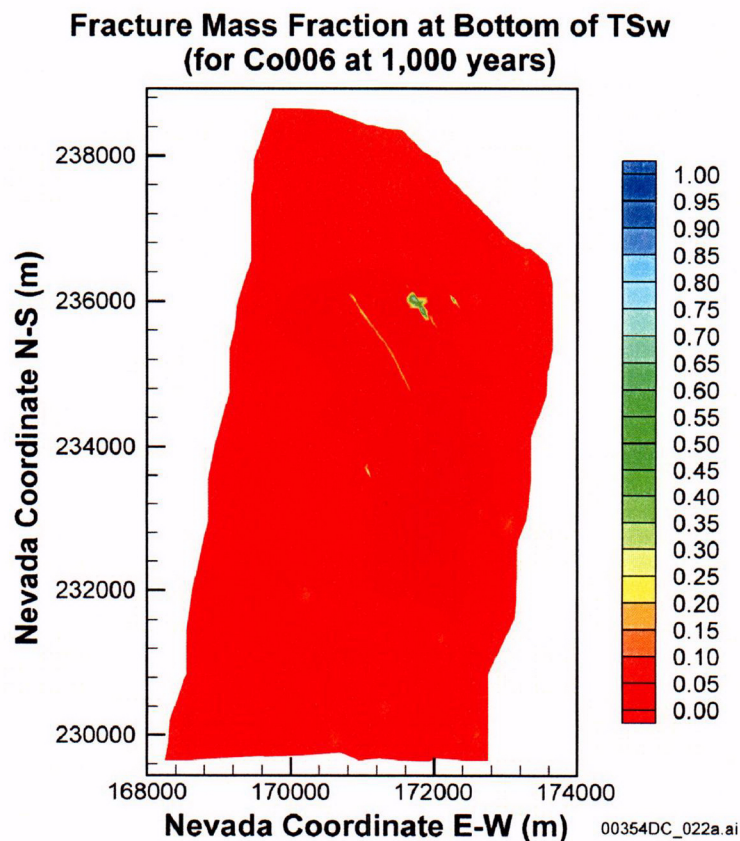
Figure 5-4. Distribution of the Relative Mass Fraction, X_R , of the 6-nm $^{239}\text{PuO}_2$ Colloid in the Fractures of the tsw39 Layer at 10 Years for the Mean Present-Day Infiltration Rate and Continuous Release

**Matrix Filtered Concentration at Bottom of TSw
(for Co006 at 10,000 years)**



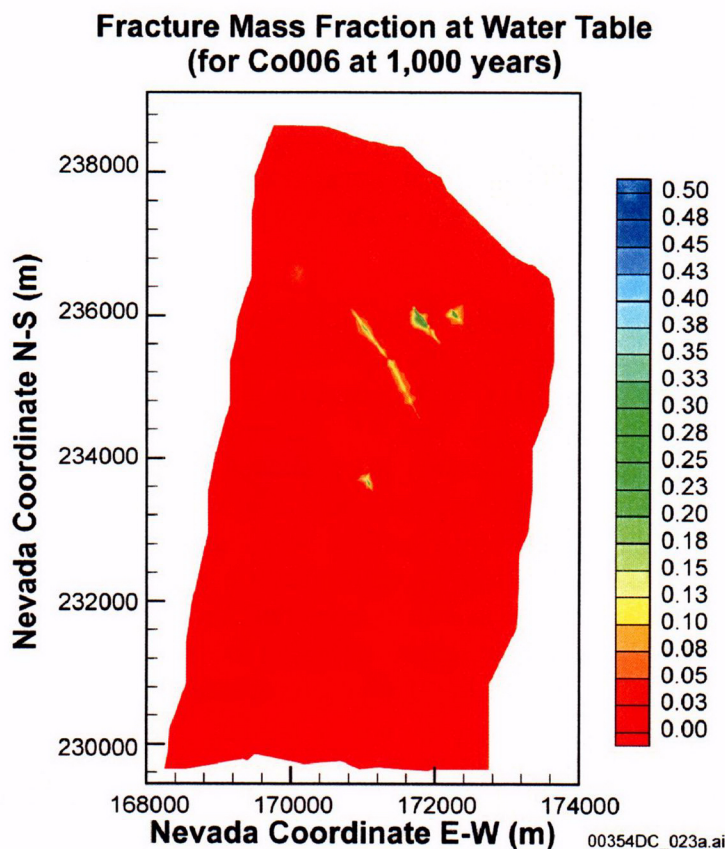
Source: BSC 2003m, Figure VI.12.

Figure 5-5. Distribution of the Relative Filtered Concentration, F_R , of the 6-nm $^{239}\text{PuO}_2$ Colloid in the Fractures of the tsw39 Layer at 10,000 Years for the Mean Present-Day Infiltration Rate and Continuous Release



Source: BSC 2003m, Figure VI.7.

Figure 5-6. Distribution of the Relative Mass Fraction, X_R , of the 6-nm $^{239}\text{PuO}_2$ Colloid in the Fractures of the tsw39 Layer at 1,000 Years for the Mean Present-Day Infiltration Rate and Continuous Release



Source: BSC 2003m, Figure VI.22.

Figure 5-7. Distribution of the Relative Mass Fraction, X_R , of the 6-nm $^{239}\text{PuO}_2$ Colloid in the Fractures Immediately above the Groundwater at 1,000 Years for the Mean Present-Day Infiltration Rate and Continuous Release

Because of its larger size, the straining is more pronounced for the 450-nm colloid than in the 6-nm colloid, and leads to higher concentrations at earlier times behind the interface. At the water table and at early times (less than 10,000 years), the maximum fracture relative mass fraction exceeds 1 (i.e., equals 1.50) because of straining (pore-size exclusion).

5.5 UNCERTAINTIES AND SENSITIVITIES

5.5.1 Uncertainties

The uncertainties related to colloid transport modeling in the unsaturated zone are summarized in the following text. The approach is to either employ conservatism in treating parameters or processes whose uncertainty is unknown or not well characterized or to capture the uncertainty through a parameter value distribution.

Colloid Retardation Kinetics—Basic knowledge about the kinetic clogging and declogging coefficients $\hat{\epsilon}^+$ and $\hat{\epsilon}^-$ is limited. Also, it is not known whether the applicability limits of the currently available kinetic models, developed from theoretical principles (Herzig et al. 1970) and tested in uniform sandy laboratory experiments (van de Weerd and Leijnse 1997) or small-scale

field tests (Harvey and Garabedian 1991), are valid under the unsaturated zone conditions at Yucca Mountain. Sensitivity analyses indicate an insensitivity of transport to the filtration parameters. In the TSPA-LA unsaturated zone transport model colloid retardation in fractures will be treated with uncertainty by sampling over a range of values based on C-Wells testing, see Section 5.7. In the TSPA-LA unsaturated zone transport model colloid matrix filtration parameters will be treated as fixed values but vary with geologic material (BSC 2003i, Section 4.2).

Effects of Matrix Diffusion on Colloidal Transport Simulation—A comparative analysis based on Case 2 (Section 5.4.3) was conducted and reported in *Radionuclide Transport Models Under Ambient Conditions* (CRWMS M&O 2000f, Section 6.17) using an earlier version of the unsaturated zone transport model. This analysis examined the transport of colloids with and without colloid matrix diffusion. The analysis indicates that diffusion is less significant in colloid transport than in solute transport, because (1) colloid diffusion is smaller than solute molecular diffusion because of the larger colloid size, and (2) size-exclusion effects at the interfaces of different geologic units further limit entry by diffusion into the matrix (especially for larger colloids). However, diffusion effects become increasingly important for a decreasing colloid size. Uncertainty in colloid matrix diffusion is treated by sampling the diffusion coefficient over a range of values in the TSPA-LA unsaturated zone transport model (BSC 2003i, Section 4.2).

Air–Water Interfaces—The affinity of colloids for air–water interfaces can have a potential effect on their transport (CRWMS M&O 2000f, Section 6.15.8). These possible effects are not currently considered in either the radionuclide transport process model or the TSPA-LA particle-tracking model. Ignoring these effects results in increased predicted migration of colloids.

5.5.2 Sensitivities

The impact of these uncertainties is assessed by estimating (1) transport for a very wide range of the kinetic filtration parameters (clogging and declogging coefficients) and (2) the impact of filtration in the fractures (by considering minor fracture filling) (BSC 2003m, Section 8.3.2.4).

Filtration Kinetics—Even though colloid retardation kinetics is uncertain, the simulations of *Radionuclide Transport Models Under Ambient Conditions* (BSC 2003m, Section 6.18) indicate that the transport is not significantly affected by varying the reverse or detachment filtration coefficient over the range from 0 to 100 percent. When there is no filtration in fractures, there is very limited retardation of the larger colloids (greater than 100 nm). However, filtration has a substantial impact on retardation of very small colloids (less than 6 nm). This is most likely a result of the larger colloids not being able to access the matrix where the filtration is assumed to occur. In this process model colloid retardation is not assumed to occur in the fractures.

Colloid Size—Colloid size is uncertain and variable and is an important parameter in describing the transport of colloids through the unsaturated zone. Travel times to the water table decrease with the colloid size: larger colloids show little retardation while very small ones are retarded significantly. Size exclusion (straining) at the interfaces of different hydrogeologic layers leads to colloid concentrations immediately above the interface that can be higher than that in the water released from the repository. This phenomenon is more pronounced in larger colloids.

Importance of Faults—The potential points of release from the repository are uncertain and may vary with time; however, this does not impact the transport of colloids. Because of the importance of transport and flow within faults on the migration of dissolved radionuclides and colloids, the impact of releasing radionuclides directly into faults was assessed (BSC 2003m, Section 6.20). Despite the importance of faults (particularly the Drillhole Wash, the Pagany Wash, and the Sundance Faults) identified in the analyses of *Radionuclide Transport Models Under Ambient Conditions* (BSC 2003m, Section 6), eliminating potential sources from the immediate vicinity of the faults has a small (even negligible) effect on transport and arrivals at the water table. This is not to suggest that faults are unimportant but only that they continue to dominate whether radionuclides are directly released into them or not.

Importance of Filtration in Fractures—The presence of fracture fill and the amount of filtration that may occur in fractures is uncertain and is evaluated for importance. The simulations of *Radionuclide Transport Models Under Ambient Conditions* (BSC 2003m, Section 6.18) indicate that when there is no fill material or filtration in the fractures, larger colloids (450 nm, 200 nm, and 100 nm) experience very limited retardation. Conversely, the retardation of the smallest colloid (6 nm) is very significant. When there is limited fill material and filtration in the fractures, the transport of the larger colloids is retarded because this filtration in the fractures becomes a dominant process retarding the larger colloids. There is not much impact on the smallest colloid particle because the small colloids can enter the matrix where substantial additional retardation takes place.

5.6 MODEL CONFIDENCE BUILDING

5.6.1 Model Validation

The colloid transport model is a submodel of the radionuclide transport model. Many other validation studies of the transport of dissolved radionuclides documented in *Radionuclide Transport Models Under Ambient Conditions* (BSC 2003m) indicate that the radionuclide transport model is adequately validated for its intended use. In addition numerous other submodels and processes which may indirectly impact the transport of colloids are also adequately validated and documented in *Radionuclide Transport Models Under Ambient Conditions* (BSC 2003m). These other processes and submodels include (1) transport of nonsorbing and nondecaying radionuclides, (2) transport of sorbing radionuclides, (3) transport involving radioactive decay chains, (4) transport in a fracture-matrix system, (5) the matrix diffusion model, (6) the sorption model, and (7) the combined matrix/active fracture model.

In general, five validation methods can be used. These are:

1. Corroboration with experimental data
2. Corroboration with data from the literature
3. Corroboration with alternative mathematical models
4. Independent technical review
5. Publication in a refereed professional journal.

The validation approach and criteria are discussed in *Technical Work Plan for: Performance Assessment Unsaturated Zone* (BSC 2002b, Section I-2-1-4), which indicates that the colloid

transport model was judged in the model validation status report (BSC 2001e, p. 28) to have been validated satisfactorily for its purposes in *Unsaturated Zone Colloid Transport Model* (CRWMS M&O 2000d). The validation was extended to the colloid transport model in the radionuclide transport model and further supported by some additional work described in *Radionuclide Transport Models Under Ambient Conditions* (BSC 2003m) and is summarized below. Despite this, there remains a lack of observational support for model validation by Methods 1 and 2 above. Methods 3, 4, and 5 are used.

Validation through Scientific Acceptance (Method 4 and 5)—Using T2R3D, Wu and Pruess (2000) studied the site-scale three-dimensional transport of radioactive solutes. Recently, Moridis et al. (2003) reported on a scientific study of site-scale three-dimensional transport of radioactive colloids in the unsaturated zone of Yucca Mountain using EOS9nT. Both studies are based on essentially the same radionuclide transport model as the one discussed here, but it involved a three-dimensional grid from the previous revision of the relevant model reports (BSC 2003m; BSC 2001c).

Additionally, EOS9nT is currently in use by Gesellschaft für Anlagen und Reaktorsicherheit (GRS) mbH, a research and engineering organization owned by the Federal Government of Germany, the State of Bavaria, the state of North Rhine-Westphalia, the Technical Inspection Organization (TÜV) and the Germanischer Lloyd. GRS has a substantial involvement in radioactivity issues, focusing on studies of the effects of potential radioactivity releases. The work of GRS using the radionuclide transport model embodied in EOS9nT is documented in two GRS reports (Javeri 2001; 2002).

Colloid and Colloid-Assisted Radionuclide Transport (Method 3)—The transport of a colloid and a solute is described in this problem. The colloid filtration (attachment) is controlled by a kinetic process. Results of the numerical model are compared to its analytical solution. The solute is radioactive and is irreversibly sorbed onto the colloid; thus, it cannot enter the liquid phase and is transported only by the mobile colloids. All the radionuclides that enter the system are sorbed onto colloids. This being the case, the radionuclide decays uniformly, and its concentration is the same on all colloids. The radionuclide concentration on each colloid is controlled by radioactive decay, and by choosing an observation time equal to $T_{1/2}$, its relative concentration is 0.5.

Properties and parameters for this problem are listed in Table 7.2-5 of *Radionuclide Transport Models Under Ambient Conditions* (BSC 2003m), and the comparison of the analytical to the numerical solutions is listed in Table 7.2-6 of *Radionuclide Transport Models Under Ambient Conditions* (BSC 2003m). Because it involves transport of a kinetically filtering colloid, T2R3D (LBNL 1999b), cannot be used for this study. The numerical results were obtained with EOS9nT (LBNL 1999a), and show nearly identical agreement with the analytical solution, while the radionuclide relative concentration on the colloids is confirmed to be a uniform 0.5.

5.6.2 Use of Analogs—Natural Analog Studies at Peña Blanca, Mexico

From the 1980s, the Nopal I uranium deposit at Peña Blanca has been recognized as a natural analog for the potential repository at Yucca Mountain (CRWMS M&O 2000g, Section 6.5.2.1). Analysis of water samples from the Nopal I uranium deposits were all super-saturated with

respect to thorium, which is attributed to the presence of colloidal thorium in the less than 0.2 μm fraction of the samples (CRWMS M&O 2000g, Section 6.5.2.15). Preliminary evidence suggests colloidal transport of thorium, protactinium, and possibly uranium (CRWMS M&O 2000g, Section 6.5.2.1.6.2), but could not be verified without studies of concentration vs. size fraction on filtered or ultrafiltered samples.

5.6.3 Alternative Conceptual Model

FEHM, V2.20 (LANL 2003, STN: 10086-2.20-00), is used for the numerical analysis of this alternate conceptual model (CRWMS M&O 2000d). FEHM calculates hydrologic flow and the transport of radionuclides, the latter by a particle-tracking algorithm. The particle-tracking method in FEHM views the computational domain as an interconnected network of fluid storage volumes. The two steps in the particle-tracking approach for steady-state flow fields are: (1) to determine the time a particle spends in a cell and (2) to determine which cell the particle travels to next. The domain can consist of a single-continuum or dual-continua (e.g., fracture plus matrix) representation of the flow field. FEHM can be used to model transport breakthrough times in porous and fractured media.

This implementation of FEHM examines a two-dimensional discrete fracture model (DFM), in which the fracture and matrix are discretely represented. This approach contains a parallel fracture that is more conservative but consistent with the dual-permeability approach used in the TSPA model. This model preceded the radionuclide transport dual continuum model. The currently accepted conceptual model for flow and transport is the dual continuum model. Even though FEHM is a continuum model, this application of FEHM is designed to simulate transport in a discrete fracture model, and it is useful to examine it as an alternate conceptual model. The discrete fracture conceptual model implemented in FEHM by itself is more conservative than the dual continuum model (CRWMS M&O 2000d). However, the FEHM implementation also considered retardation of colloids in the fractures based on C-Wells data as described below. As the results of the FEHM modeling will show, initial breakthrough times are delayed compared to the predictions with the radionuclide transport model, which does not consider retardation of colloids in the fractures. These differences provide insight into the behavior of the transport of colloids (particularly waste-form colloids) obtained from this alternative model documented in *Unsaturated Zone Colloid Transport Model* (CRWMS M&O 2000d).

The objectives of this modeling include the following:

1. Use of a process level model to evaluate the potential mechanisms for colloid transport at Yucca Mountain
2. Provide ranges of parameters for significant colloid transport processes to performance assessment for the unsaturated zone
3. Provide a basis for development of an abstracted model for use in performance assessment calculations.

The details of the assumptions, conceptualization, implementation into a numerical model, data, validation, results, and analyses are presented in *Unsaturated Zone Colloid Transport Model*

(CRWMS M&O 2000d, Section 6). A summary to the information extracted from this reference is provided below.

Stratigraphy, Numerical Grid, and Boundary Conditions—A simplified stratigraphy that contains three hydrogeologic units, the Topopah Spring welded (referred to in this report as TSw4), Calico Hills vitric (CH1v), and Calico Hills zeolitic (CH1z), was used in the numerical analysis. These units are equivalent to those considered in abstraction of transport properties for TSPA for the site recommendation (CRWMS M&O 2000h, Section 6.4). The hydraulic properties for these units were derived from DTN: LB970601233129.001 (the properties of TSw4 were assigned to the tsw34 model unit). The grid extends from 630 m to 1,150 m and models the half distance between fractures, which was 10 m (i.e., the grid is 5 m wide). This distance corresponds to the fracture spacing for the CH2v to CH5v and CH2z to CH5z units. The lower boundary was selected to be 100 m below the water table to isolate detailed flow conditions related to the boundary from the model domain of interest. The upper elevation boundary represents approximately the top of the TSw4. The fracture width is 1 mm based on estimates from the active fracture model developed in *Particle Tracking Model and Abstraction of Transport Processes* (CRWMS M&O 2000h, Section 6.2.1), which used data in DTN: LB990501233129.001 to derive the parameters. The vertical grid spacing is 2.5 m. The horizontal grid spacing is variable and extends from 1 mm to 80 cm.

A flux of 5 mm/year (DTN: LB990801233129.003) averaged over the top surface of the model is injected into the fracture only at the top of the model. This allows the redistribution of flow to occur above the repository level (1,087 m) such that the flow field relevant to transport is parallel in the fracture and matrix units and is at steady state conditions for the transport simulations. In general, the flow through the system simulates fracture flow in the TSw4, the transition to predominately matrix flow in the CH1v, and matrix flow in the CH1z. The simulations are unsaturated and do not consider perched water systems. Release of actinides or colloids occurs at the repository level. This model examines important mechanisms for colloid transport that will need to be incorporated into a performance assessment calculation and is not intended to represent the site scale or what happens on the site scale.

Pore Size Exclusion—The model considered pore size exclusion of colloids from the fractures to the matrix based on estimates of the pore size distributions for the three units considered in the model. These estimates were obtained from the moisture retention curves (DTN: GS980908312242.039; GS950608312231.008) judged to be representative of the site.

The percent of colloids that could enter a unit was then determined based on the percent of pore sizes above and below the colloid size of interest (6 to 450 nm in this study) for the three units considered in the analysis. This approach results in, for example, in the TSw4, only five percent of the 450-nm colloids can enter the matrix versus 65 percent of the 6-nm colloids. This fact has a couple of implications, depending on the unit through which the colloids are transported. For the case in which fracture flow is dominant, large colloids can experience size exclusion from the matrix, which causes them to stay in the fracture, and smaller colloids can enter the matrix, which will increase their residence time in the system. In contrast, for the case in which matrix flow is dominant, large colloids that cannot enter the matrix are physically removed at the interface between the fracture and matrix or between different matrix units as a filter cake.

Source Term—The actinide source term was based on the 10,000-year radionuclide release at the edge of the engineered barrier system from an expected value run for the TSPA for the Viability Assessment (DOE 1998). Actinide release started at 1,000 years and was continuous until 10,000 years, the duration of the simulated time.

The transport of both natural colloids and waste form colloids were considered. The waste-form colloid concentration was held constant at 6×10^{-8} M, which is the high end of the concentration measurement from DTN: LL991109751021.094.

Natural colloids are formed as the weathered by-products of the host material and are ubiquitous in nature. Multiple measurements have been done for groundwater samples at Yucca Mountain and other areas on the Nevada Test Site. The measured particle concentrations that are used vary between 1.05×10^6 and 2.72×10^{10} particles/mL, with the lowest being for water from well J-13 and the highest for water from well U19 on Pahute Mesa.

Conceptual Picture of the Matrix—Conceptually, the matrix in the unsaturated zone will have several different effects on colloid transport, depending on the unit being considered. In general, primary colloid removal in the matrix will be due to physical effects, such as small pore sizes and low volumetric water content. Chemical removal could occur onto mineral surfaces, but it is assumed that the far-field geochemistry will not vary significantly from current conditions, and therefore, chemical removal in the matrix is expected to be small. Specifically, the TSw4 has a very small pore-size distribution and is expected to limit the number of colloids that enter the matrix. Size exclusion will force the majority of the colloids to remain in the fractures in this unit, and the small percent of colloids that do enter the matrix will have a high probability of being retained due to filtration in the matrix and at the interfaces between units. For the CH1v, matrix flow is dominant, the pore sizes are large, and the majority of colloids will be able to enter the matrix due to imbibition. Physical removal of colloids in this unit is likely because the matrix is more tortuous than the fractures and variable pore sizes. The base unit in the model is the CH1z, which has a smaller pore-size distribution than the CH1v. This fact is important because it is expected that a significant quantity of colloids could be filtered at the interface between the two units. The CH1z will also exhibit size exclusion between the fracture and matrix unit for larger colloids.

Colloid Transport in Fractures—Retardation of colloids in the fractures was considered and was based on available data at the time from the C-Wells tracer experiments using microspheres. For flow in a fracture, an equilibrium relationship between the forward and reverse rate was used which is dependent on the half aperture of the fracture and the bulk density. For example, in the C-Wells analysis, the reverse rate is reported as a function of the fracture aperture (Reimus et al. 1999).

Based on the range of forward rates estimated from C-Wells for the Bullfrog and Prow Pass units, a range of forward rates that varied between 0.001 and 0.5 hr^{-1} was considered (Reimus et al. 1999; DTN: LA9912PR831231.006). The reverse rates considered varied between 0.001 and 4 hr^{-1} . Simulation results on the microsphere breakthrough from C-Wells completed after this analysis was reported indicate that the reverse rates multiplied by the fracture half aperture vary between 0.0001 to 3.33 hr^{-1} (Reimus et al. 1999; DTN: LA9912PR831231.006). This

indicates that the reverse rate could be an order of magnitude smaller than considered in this analysis. Various combinations of forward and reverse rates were used in the analysis.

Plutonium Sorption/Desorption onto Natural Colloids—A kinetic sorption model was used for the preliminary analysis of Pu(IV) and Pu(V) sorption and desorption onto colloidal matter. Preliminary curve fitting results of laboratory data on the sorption of plutonium onto clay colloids was used for numerical modeling (DTN: LA0003NL831352.001). Data were also available on the sorption of plutonium onto silica colloids.

The results of the curve fitting yielded forward rates on the order of one. The reverse rates are around 1×10^{-5} . Sorption is clearly very rapid, whereas desorption is very slow from the clay colloid material.

Results—The results of the simulation of this model indicate initial breakthrough of about 1,500 years for colloids of size 450 nm and 1,700 years for colloids of size 6 nm. These breakthroughs are significantly delayed compared to the results of the radionuclide transport model in Section 5.4.3.

A number of sensitivity studies were done with this model to evaluate the impact on release from (1) pore size exclusion from the matrix in fracture dominated flow, (2) colloid removal at matrix/fracture interface in matrix dominated flow, (3) source term (release rate), (4) colloid retardation, and (5) reversible sorption of radionuclides onto colloids. They are not discussed here as the focus is on the currently accepted model for colloid transport in the unsaturated zone.

The conclusions of this alternate model indicate that waste-form colloids can be transported through the unsaturated zone. The size-exclusion mechanism that forces colloids to remain in the fractures enhances transport in rock units with fracture flow and retards transport in units where matrix flow dominates because there is no advective flux in the fracture to move the colloids.

The FEHM modeling and analysis indicate that some colloids, particularly waste-form colloids or natural colloids with kinetically controlled actinide sorption/desorption, could enhance actinide transport. Colloid facilitated transport in the unsaturated zone is currently screened in the TSPA-LA.

5.7 TSPA-LA IMPLEMENTATION OF UNSATURATED ZONE TRANSPORT

The radionuclide transport model process model is intended to establish the technical basis for unsaturated zone transport that is carried through into the TSPA-LA model through an abstraction based on FEHM particle tracking. This section outlines some important differences and similarities between the radionuclide transport model process model and the TSPA-LA particle-tracking abstraction. The computer software code on which the unsaturated zone transport abstraction model is based is FEHM, Version 2.21 (STN: TBD). Details of the model, assumptions, development, input, and example results are provided in *Particle Tracking Model and Abstraction of Transport Processes* (BSC 2003i). The information presented here focuses on processes that uniquely affect the transport of colloids.

5.7.1 Background

Particle-tracking transport models take a fundamentally different approach than the finite difference models (radionuclide transport model) in their solution of the advective-dispersion equations. The trajectory of individual molecules or packets of fluid containing molecules are tracked through the model domain. In a typical particle-tracking algorithm, a particle is sent to a new position assuming that the magnitude and direction of the velocity vector are constant during a time step. Dispersion is treated as a random process that diverts the particle a random distance from its dispersion-free, deterministic path. Linear equilibrium sorption can be handled through the use of a retardation factor to correct the magnitude of the particle velocity. Particle tracking solutions do not suffer from numerical dispersion compared to finite difference or finite element representations of the advection-dispersion equations.

In the TSPA-LA unsaturated zone transport model, a particle-tracking technique is employed that can be used for transient, multi-dimensional finite-difference or finite-element codes. The algorithm is designed for computing solute concentration fields quickly and easily with structured or unstructured numerical grids of arbitrary complexity. Both continuum and dual-permeability formulations can be simulated. This flexibility is accomplished by extending the cell-based strategy of Desbarats (1990) for mapping out the path of the particle. In this method, the calculation of an "exact" pathline is replaced with a cell-to-cell migration of the particle. The mass flux from cell to cell is used directly, and no velocity interpolations are required. Since numerical solutions for fluid flow are typically mass conservative (though not necessarily accurate) the particle-tracking method automatically conserves mass.

As discussed in Section 5.4.1 of this report, radionuclides may have either reversible or irreversible interactions with colloids. The abstraction model for unsaturated zone transport treats colloid facilitated transport for both kinds of interactions. Most radionuclides are assumed to sorb onto colloids reversibly (that is, they have measurable desorption rates and can be entirely desorbed from the colloids) (BSC 2003f, Section 6.3.3.1). However, plutonium and americium can sorb either reversibly or irreversibly onto colloids with the relative percentages of these obtained from an analysis of waste-form degradation and waste package corrosion processes occurring in the repository near-field environment (BSC 2003f, Section 6.3.3.1). In general, the majority of plutonium and americium sorbed to colloids is irreversible, with a typical percentage being 90 to 99 percent irreversible and 1 to 10 percent reversible (BSC 2003f, Section 6.3.3.2, p. 74). Irreversibly sorbed plutonium and americium are either embedded in the waste-form colloids (e.g., smectite colloids formed by degradation of high-level radioactive waste glass) or are so strongly sorbed onto colloids (e.g., iron oxyhydroxide colloids formed by corrosion of waste packages) that there is no detachment for typical transport time scales (thousands of years) through the unsaturated zone. By definition, the irreversibly sorbed plutonium and americium transport in a manner identical to the colloids onto which they are sorbed. Note that *EBS Radionuclide Transport Abstraction* (BSC 2001a), specifically Attachment II, discusses the mathematical implementation for irreversible sorption of plutonium and americium onto iron oxyhydroxide colloids in the engineered barrier system.

5.7.2 Comparison of Assumptions

The assumptions taken to develop the unsaturated zone radionuclide transport abstraction model are outlined in detail along with their rationale as the first step toward developing the computational and mathematical models needed in radionuclide transport calculations for the TSPA model. A subset of those assumptions is listed here for the purpose of indicating any differences between the radionuclide transport model process model and the particle-tracking model to be used in the TSPA-LA.

- Assumption 1:** The active fracture model appropriately accounts for reduced fracture/matrix interaction. The radionuclide transport model uses the active fracture model formulation.
- Assumption 2:** The influence of matrix diffusion in a dual-permeability system can be handled with a sub-grid-block model consisting of parallel flow in a discrete fracture and connected matrix. The radionuclide transport model considers matrix diffusion for both dissolved species and colloids. The abstraction model treats aqueous radionuclide diffusion between fractures and the matrix, but conservatively neglects colloid fracture-matrix interaction through diffusion.
- Assumption 3:** Radionuclide sorption can be approximated with a linear, equilibrium sorption model characterized by a single parameter, the distribution coefficient, K_d . Radionuclide transport model makes the same assumption.
- Assumption 4:** Dispersion of both aqueous and colloidal species can be approximated as consisting only of longitudinal dispersion, characterized by a constant value of the dispersivity, α_L . Same assumption is made in the radionuclide transport modeling.
- Assumption 5:** For the abstraction model, radionuclide mass sorbs reversibly to nondiffusing colloids with a constant equilibrium sorption parameter $K_c = C_{coll}/C_{fluid}$, where C_{coll} is the radionuclide concentration residing on the colloids (moles radionuclide on colloid per kilogram of fluid), and C_{fluid} is the corresponding concentration in the fluid phase (moles aqueous radionuclide per kilogram of fluid). The same assumption is made in the radionuclide transport modeling. Note that the radionuclide transport model does not address reversible colloid-facilitated radionuclide transport. It only considers irreversibly sorbed radionuclides on colloids.
- Assumption 6:** In the abstraction model, two groupings of colloids are considered for radionuclides with irreversible attachment to colloids: "irreversible fast colloids", which are assumed not to be affected by retardation in fractures and irreversible slow colloids which are affected by retardation in fractures. The fraction of colloids that is the former results from the C-Wells testing. The radionuclide transport model only considered retardation in fractures as a sensitivity case (see Section 5.5.2 in this report).

Assumption 7: In the abstraction model, colloids with irreversibly attached radionuclides undergo irreversible filtration in the matrix based on size exclusion at interfaces between different matrix units. Size exclusion filtration is also treated in the radionuclide transport model.

Assumption 8: For the purposes of computing radionuclide transport, flow through the unsaturated zone can be approximated assuming that the system (rock mass and flow conditions) has not been influenced by repository waste heat effects. Durable changes to the rock mass hydrologic properties are also assumed to be negligible. The same assumption is made in the radionuclide transport modeling.

Assumption 9: Climate changes can be considered in an approximate way by imparting an instantaneous jump from one steady state flow field to another, with a corresponding rise or fall in the water table representing the bottom of the unsaturated zone model. Shorter-term transients (wet and dry years, individual storm events, etc.) are assumed to be adequately captured with a model that assumes such transients can be averaged to obtain a long-term, effective steady state. The same assumption is made in the radionuclide transport modeling.

In addition to the difference in modeling approaches (particle-tracking vs. finite difference), Assumption 6 is treated differently between the TSPA-LA unsaturated zone transport model and the radionuclide transport model. The implication of this assumption on colloid transport is important and is discussed here. Results from the radionuclide transport model, which ignores retardation of colloids in fractures, indicate very rapid colloid migration through the unsaturated zone (Figures 5-2 and 5-3). Results from the saturated zone transport model, which includes retardation of colloids in fractures based on the C-Wells testing, indicate significant attenuation of colloids and slow colloid migration through the unsaturated zone (see Section 6.4, Figures 6-5 and 6-6). It is highly likely that the primary reason for this different behavior is in the different treatment for colloid retardation in fractures. The TSPA-LA model for unsaturated zone transport considers retardation of colloids in fractures based on the C-Wells testing. This results in significant retardation of colloids compared to the result of the radionuclide transport model.

The application of colloid retardation data from testing done under saturated conditions to similar rock under unsaturated conditions can be justified. Literature suggests that colloid transport is more attenuated under unsaturated zone conditions (Wan and Wilson 1994). For instance, it is common practice for experimentalists studying unsaturated zone colloid transport to also run experiments under saturated conditions in the same or similar laboratory apparatuses; and in virtually all cases, there is greater attenuation under unsaturated zone conditions. There are several reasons why using the same distribution in the unsaturated zone as the saturated zone should be conservative:

1. Experimental and field evidence indicates less colloid transport under unsaturated conditions compared to saturated conditions (mainly because of air-water interfaces) (Wan and Wilson 1994).

2. Slower flow under unsaturated conditions results in longer times for retardation to take place.
3. Greater ionic strengths in unsaturated zone pore waters should tend to destabilize colloids resulting in greater retardation.
4. All processes operating to retard colloids under saturated zone conditions are also operable under unsaturated zone conditions.
5. Additional unsaturated zone processes that do not operate in the saturated zone can also retard colloids in the unsaturated zone, such as capture at the air–water interface and film straining (Wan and Tokunaga 1997).

A possible but highly unlikely process that could result in less retardation in the unsaturated zone than saturated zone is associated with episodic flow. Episodic flow in the unsaturated zone could result in film flow in fractures where the air–water interfaces become mobile. Such events could enhance the detachment of colloids from surfaces because air–water interfaces will sweep surfaces. This could enhance colloid transport relative to the saturated zone. It seems very unlikely that film flow with a continuous air–water interface could be sustained over very large distances and for very long times in the unsaturated zone for a number of reasons:

1. Any place that the film encounters a “pinch-point” in a fracture where the film thickness exceeds fracture aperture, the film will “bridge” the aperture and a discontinuity in the air–water interface will occur.
2. Films also will flow only as long as the matrix is very close to full saturation. If this is not the case, capillary suction in the unsaturated matrix will draw the water out of the fractures and effectively stop the film from advancing. It would take a very long and sustained flow transient to effectively establish film flow for very long distances in the unsaturated zone. Once the film flow dies out, the water (and colloids) will either slow down dramatically or be imbibed into the matrix where other retarding processes occur.

5.7.3 Example Results and Conclusions from TSPA-LA Unsaturated Zone Transport Model

While results are presented in *Particle Tracking Model and Abstraction of Transport Processes* (BSC 2003i, Figures 6-16 and 6-17) for the breakthrough curves of 36 radionuclides under present-day and glacial infiltration, the contributions of dissolved vs. colloidal species are not broken out and presented. Only qualitative statements are made in *Particle Tracking Model and Abstraction of Transport Processes* (BSC 2003i) concerning the observed model behavior of colloid transport:

1. “The simulation results reveal that irreversible fast colloids (which are assumed not affected by matrix diffusion and retardation) have the shortest breakthrough times and the greatest breakthrough quantities. Within a time period of far less than 100 years, more than 50 percent of the irreversible fast colloids traveled through the UZ.”

2. "Irreversible slow colloids which undergo retardation moved slower than their corresponding fast colloids but faster than their corresponding dissolved species. The travel time of the irreversible slow colloids depends on their retardation factor. In TSPA-LA simulations, the retardation factors of the slow colloids will be sampled and its impact on system performance will be evaluated."
3. "With regard to colloid transport, the simulation results show that current conceptualizations suggest that colloids can play an important role in accelerating the transport of radionuclides in the UZ, especially the irreversible fast colloids. Of course, if the quantity of irreversible fast colloids is low, the impact on dose would not be expected to be important."
4. "In TSPA-LA calculations, a conservative percentage of irreversible fast colloids will be selected to study its impact on dose. For irreversible slow colloids, the retardation factor will be sampled to investigate parameter uncertainty on system performance."

5.8 SUMMARY OF UNSATURATED ZONE SCREENING ARGUMENTS

Colloid transport through the unsaturated zone at Yucca Mountain is expected to be primarily through fractures because of pore-exclusion effects. The assumption made in the radionuclide transport model process that no colloid sorption will occur in fractures or along their walls is very conservative and contrary to evidence from the C-Wells test in the volcanics of the saturated zone (BSC 2003b). These tests indicate a very large degree of colloid sorption and result in significant delays on arrival times (BSC 2003a). This ignoring of colloid sorption in the fractures is largely responsible for the rapid travel times through the unsaturated zone predicted by the radionuclide transport model and shown in Figures 5-2 and 5-3.

Because the radionuclide transport model does not consider retardation of colloids in the fractures of the unsaturated zone and because larger colloids (greater than 6 nm) have difficulty entering the matrix surrounding the fractures in the zeolitic portions of the TSw, colloids are predicted to travel quickly through the zeolitic regions of the unsaturated zone beneath the repository by this model. However, the radionuclide transport model does show that colloid transport is retarded at the interface of the zeolitic portion of the TSw and underlying CHn layers as well as at the unsaturated zone and underlying saturated zone interface. The results summarized in Section 5.4.3 show a significant build up of colloids at these interfaces. This is a result of the relatively small pore size and permeability of the underlying layers at each interface compared to that of the overlying layers. Because of this, colloids cannot be transported through the interface at the same rate at which they are transported to the interface. This filtering mechanism is important in retarding the migration of colloids through the unsaturated zone.

The role of the air-water interface on enhancing or retarding colloid transport is determined by the affinity of colloids to the interface and the degree of saturation. Based on the current understanding, it is assumed that the tendency of the air-water interface will be to retard colloid transport.

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6. COLLOID TRANSPORT IN THE SATURATED ZONE

This section summarizes the current state of knowledge concerning the transport of colloids in the saturated zone and their release into the biosphere. The saturated zone is the fourth of the repository system subfeatures examined to determine the importance of colloids with respect to the postclosure performance of the Yucca Mountain repository, as shown in Figure 1-1. Modeling assumptions to be used in the TSPA-LA are discussed. The information presented in this section primarily draws on the discussion contained in the following YMP sources:

- *Site-Scale Saturated Zone Transport* (BSC 2003a).
- *Saturated Zone Colloid Transport* (BSC 2003b).

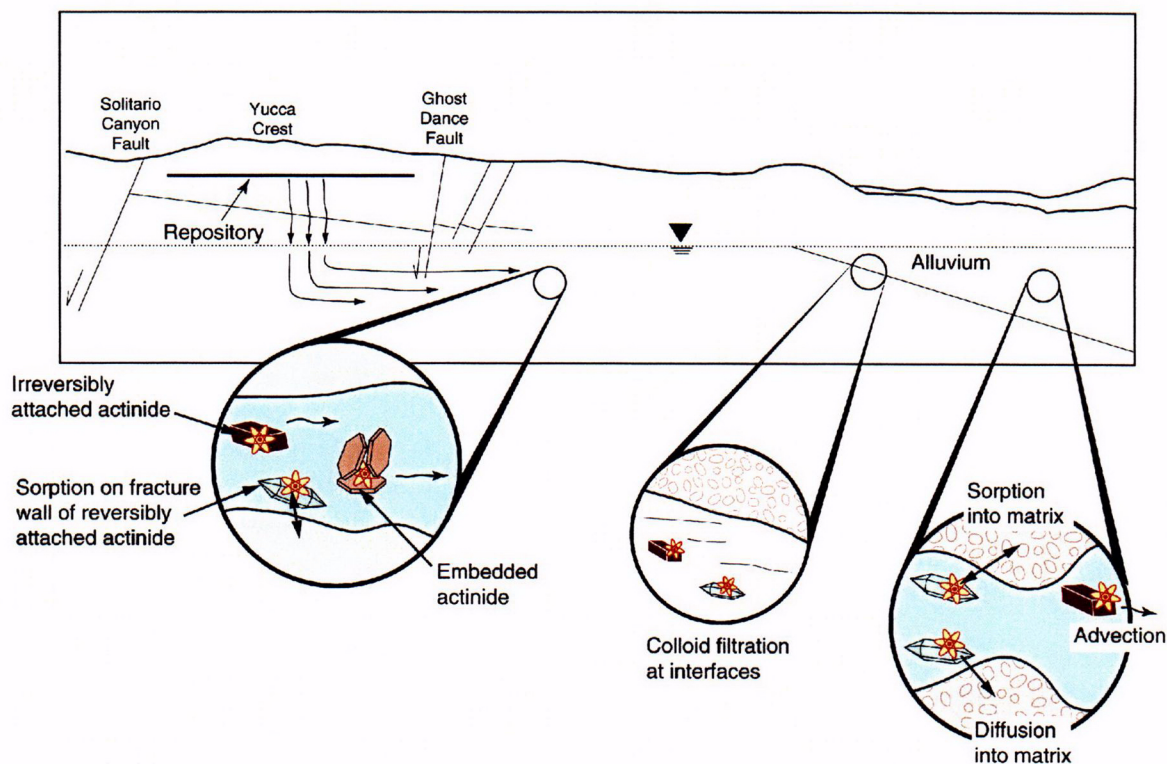
This chapter is organized in the following way: Section 6.1 describes the relevant processes for describing colloid and colloid-facilitated transport in the saturated zone, and Sections 6.2 through 6.7 describe the saturated zone TSPA model for radionuclides sorbed reversibly and irreversibly to colloids, data and validation. Unlike in Section 5 (the discussion of the unsaturated zone, there is no distinction between the process model and the TSPA model for the saturated zone.

6.1 DESCRIPTION OF RELEVANT PROCESSES

The base-case conceptual model for saturated zone transport begins in the neighborhood of the repository footprint at the water table and ends at the compliance boundary downstream from this footprint. As shown schematically in Figure 6-1, the flow path from the potential repository to the compliance boundary begins in the volcanic tuffs but ends in the alluvium with different transport processes operating in the volcanic tuffs and the alluvium. The compliance boundary corresponds to the far right edge of the figure and is located 18 km downgradient of the saturated zone under the repository.

The colloid related aspects of this conceptualization are as follows:

1. Radionuclides can undergo colloid-facilitated transport in the volcanics. Radionuclide affected colloids, which are transported to the saturated zone, may include the types shown in Figure 6-1 (i.e., natural colloids [typically clay or silica]), waste-form colloids resulting from degradation of spent fuel or glass, and iron oxyhydroxide colloids resulting from degradation of the waste container. The transport of colloids themselves in groundwater, as well as the mechanisms of sorption of radionuclides onto these colloid particles, is included in the transport model for the saturated zone. Mechanisms for transport of colloid particles in groundwater are considered in detail in *Saturated Zone Colloid Transport* (BSC 2003b). Movement of colloids occurs within fractures only. Due to the relatively large size of the colloids, matrix diffusion of these particles is negligible. Colloid attachment and detachment to fracture surfaces is modeled by first-order rate expressions. Radionuclides, which are reversibly adsorbed onto colloids, are modeled using the K_c model, which represents the equilibrium partitioning of radionuclides between the aqueous phase and the colloidal phase with the distribution coefficient K_c (CRWMS M&O 1997, Equation 8-10, p. 8-35).



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Figure 6-1. Transport Processes Relevant to Colloid Transport in the Saturated Zone

2. Radionuclides can undergo colloid-facilitated transport in alluvium. The conceptual model for colloid-facilitated transport in the alluvium is essentially the same as in fractured tuffs in that colloids are modeled as transported only by advective water (no diffusion into stagnant water or into grains). Colloid attachment and detachment onto alluvial surfaces are described by first-order rate expressions. Laboratory site-specific data for colloid transport in the alluvium along with literature data are used to obtain distributions and bounds for attachment and detachment rate constants (BSC 2003b). As in the case of colloid transport in fractured tuffs, it was shown (CRWMS M&O 2001c) that the local equilibrium assumption is valid for all but the shortest transport times and is expected to overestimate transport mobility of radionuclides for those shortest transport times.

6.2 MODEL ASSUMPTIONS

In the unsaturated zone transport and TSPA model, most radionuclides are assumed to sorb onto colloids reversibly (that is, they have measurable desorption rates and can be entirely desorbed from colloids) (BSC 2003f, Section 6.3.3.1). However, plutonium and americium can sorb either reversibly or irreversibly onto colloids with the relative percentages of these obtained from an analysis of waste-form degradation and waste-package corrosion processes occurring in the repository near-field environment (BSC 2003f, Section 6.3.3.1). In general, the majority of the plutonium and americium sorbed to colloids is irreversibly sorbed, with a typical percentage

being 90 to 99 percent irreversible and 1 to 10 percent reversible (BSC 2003f, Section 6.3.3.2, p. 74). Irreversibly sorbed plutonium and americium are either embedded in waste-form colloids (e.g., smectite colloids formed by degradation of high-level radioactive waste glass) or are so strongly sorbed onto colloids (e.g., iron oxyhydroxide colloids formed by corrosion of waste packages) that there is no possibility of detachment for typical transport time scales (thousands of years) through the saturated zone. Note that the *EBS Radionuclide Transport Abstraction* (BSC 2001a), specifically Attachment II, discusses the mathematical implementation for irreversible sorption of plutonium and americium onto iron oxyhydroxide colloids in the engineered barrier system.

By definition, the irreversibly sorbed plutonium and americium transport in a manner identical to the colloids onto which they are sorbed. Therefore, the colloid retardation factor uncertainty distributions developed in this analysis are necessary to describe the transport of the irreversibly sorbed radionuclides. Several field observations have suggested that a small percentage of colloids are transported with essentially no retardation in groundwater (Kersting et al. 1999, p. 56; Penrose et al. 1990, p. 228), whereas the majority undergoes either reversible or irreversible filtration, which can be described by a retardation factor, R_{col} . The value of R_{col} is dependent on several factors such as colloid size, colloid type, and geochemical conditions (e.g., pH, Eh, and ionic strength). These factors are folded into the distribution of R_{col} that has been developed from field and experimental data collected under varying geochemical conditions with different colloid types and sizes. Attachment rate constants, k_{att} , and detachment rate constants, k_{det} , of colloids to the rock matrix have been measured, and separate R_{col} uncertainty distributions have been developed for the fractured volcanics and the alluvium.

The attachment rate constant is also used to determine the fraction of the colloids that transport with no retardation. Specifically, the inverse of the attachment rate constant provides a measure of the reaction time scale. Colloids for which this reaction time scale is smaller than the travel time through the system will transport with no retardation. The following sections document the development of R_{col} uncertainty distributions for the volcanics and the alluvium as well as the fraction of colloids that transport unretarded.

6.3 DATA AND TESTING FOR DETERMINING COLLOID RETARDATION FACTORS FOR IRREVERSIBLY SORBED RADIONUCLIDES

6.3.1 Data

The base case flow model (DTN: LA0304TM831231.002) was used directly as an input to the base-case transport model. For most parameters, the base-case value was chosen to be the median of the uncertainty distribution, except for the sorption coefficient of dissolved radionuclides, which was assigned a value of 0 for the base case, which leads to faster transit times for the base case than the stochastic simulations. The flow model provides the numerical grid with geometric coefficients and the groundwater flow velocity field which are used by the transport model.

The input parameters, which are considered uncertain, for the base-case transport model (DTN: LA0304SK831231.001) are:

1. Colloid retardation factor in volcanics for irreversible colloids;
2. Groundwater concentration of colloids for calculating the relative concentration of radionuclide on colloids, needed for colloid facilitated reversible transport;
3. Sorption coefficient onto colloids for calculating the relative concentration of radionuclide on colloids, needed for colloid facilitated reversible transport;
4. Fraction of colloids transported unretarded for post processing the breakthrough curves generated by the transport model; and
5. Colloid retardation factor in alluvium for irreversible colloids for calculating the colloid sorption coefficient.

For each parameter, the rationale for the selection of the range of values, probability distribution, and expected value are presented summarized in the following sections. Details are given in *Saturated Zone Flow and Transport Model Abstraction* (BSC 2003c).

6.3.2 Testing

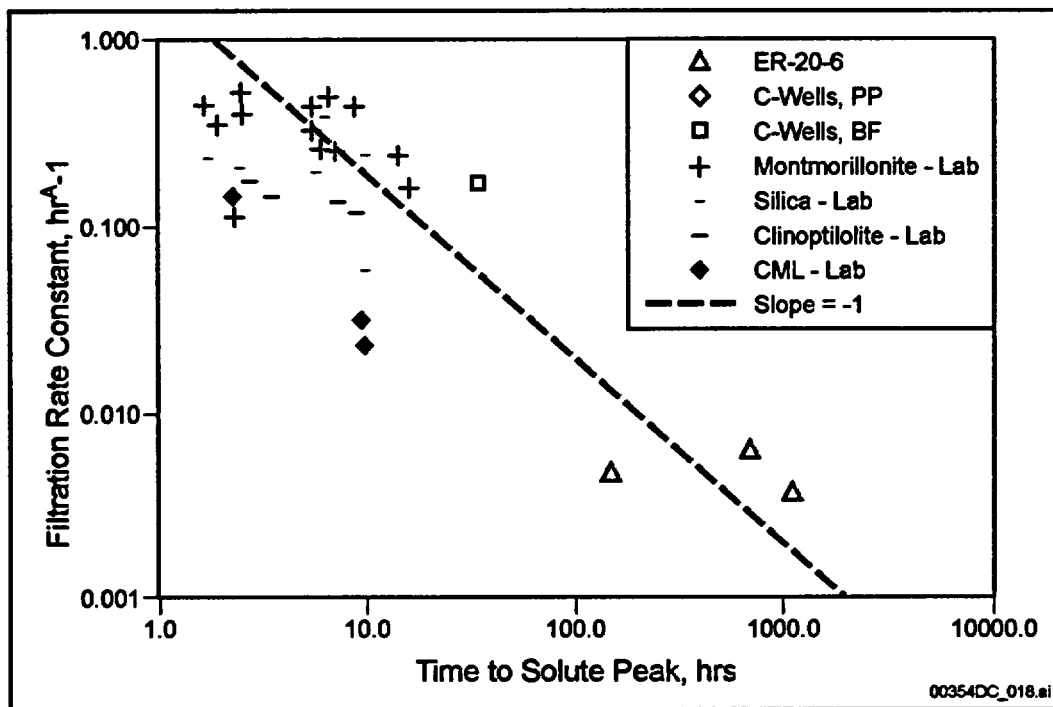
6.3.2.1 Colloid Transport in Fractured Tuff

Test Description—Colloid filtration rate constants and retardation factors for the fractured volcanics have been estimated in a number of laboratory and field experiments conducted for the YMP and the Underground Test Area project. All of the field measurements have involved fluorescent CML microspheres ranging in size from 280 to 830 nm in diameter. Laboratory fracture experiments have been conducted using silica, montmorillonite, and clinoptilolite colloids in addition to CML microspheres. In one study, silica colloid transport (~100-nm diameter) was compared directly with CML microsphere transport (330-nm diameter), and it was found that the microspheres transported conservatively relative to the silica colloids (Anghel 2001, Chapter 6). This result suggests that colloid filtration and retardation parameters derived from CML microsphere responses in field tracer tests should be conservative if used to predict natural inorganic colloid transport in fractured systems.

Colloid filtration and detachment rate constants have been derived from colloid responses in tracer tests by using the advection-dispersion equation with appropriate terms for a single reversible first-order reaction to account for mass transfer between mobile water and immobile surfaces (filtration and detachment) to fit the data. Details of the interpretation procedure for the tests are provided in *Site-Scale Saturated Zone Transport* (BSC 2003a).

Test Results: Colloid Filtration Rate Constants for Fractured Volcanics—Filtration rate constants are obtained from interpretations of several field and laboratory tracer tests conducted in saturated fractured rocks as a function of the time to reach peak nonsorbing solute concentrations in the tests (Figure 6-2). The filtration rate constants reflect the fraction of colloids that were not filtered during the tests; that is, the rate constant is constrained primarily

by the magnitude of the early arrival of colloids. The figure also shows that, even though different sizes and types of colloids were used in the different tests, there is an apparent trend of decreasing filtration rate constant with residence time. The line drawn through the data (not a fit) has a slope of -1 , which implies an inverse time dependence of the filtration rate constant.



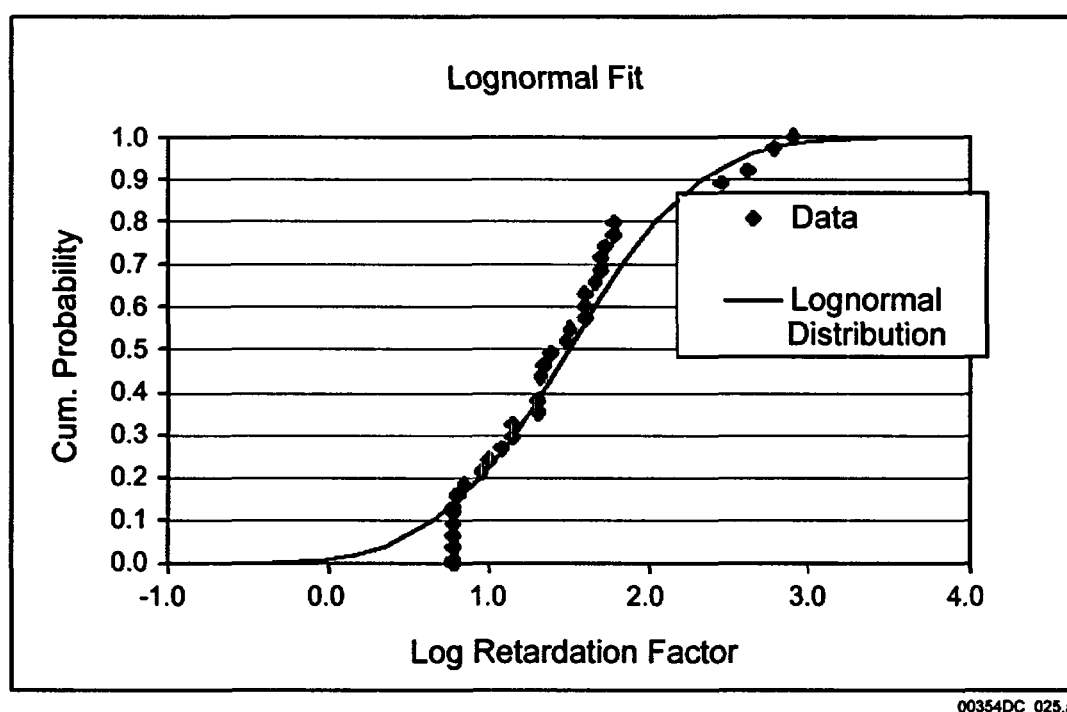
Source: BSC 2003b, Figure 1. DTNs: LA0007PR831231.001 (C-Wells BF data); LAPR831231AQ99.001 (C-Wells PP data); LA0302PR831352.002 (ER-20-6 well 3 data); LA0302PR831352.001 (ER-20-6 well 2 data); LA0302PR831231.003 (non-Q) (ER-20-6 well 3 solute data); LA0302PR831231.002 (non-Q) (ER-20-6 well 2 solute data); LA0301PR831352.001 (silica and CML data); LA0301PR831361.003 (silica and montmorillonite data); LA0301PR831361.004 (montmorillonite and clinoptilolite data); LA0303PR831231.003 (analysis of C-Wells rate constants); LA0303PR831352.002 (analysis of ER-20-6 rate constants); LA0303PR831352.003 (analysis of laboratory rate constants).

Figure 6-2. CML Microsphere and Inorganic Colloid Filtration Rate Constants (1/hr.) as a Function of Time to Solute Peak Concentration in Several Field and Laboratory Tracer Tests in Saturated Fractured Media

The results suggest that some fraction of colloids may always transport through a fracture flow system regardless of the time or length scale of the observations. It is tempting to draw the conclusion that filtration rate constants will continually decrease with increasing time scales. However, it may be more appropriate to consider the possibility that, while the majority of colloids might be filtered quite quickly, the field tests show that there is a small fraction that are resistant to filtration and, therefore, capable of traveling large distances over long time periods. This statement implies that there may be a distribution of colloid filtration rate constants rather than a fixed rate constant that applies to all colloids. The appearance of a small fraction of colloids at about the same time as nonsorbing solutes in tracer tests, regardless of the overall time scale of the test, forces filtration rate constants to decrease with time when single rate constants are assumed to apply to all colloids.

Ignoring the possible scale effect, a cumulative probability distribution function for the filtration rate constants is derived from the experimental results.

Test Results: Colloid Retardation Factors for Fractured Volcanics—Colloid retardation factors, R_{col} , are then calculated from colloid filtration and detachment rate constants using the interpretive results from the tests (Figure 6-3).



Source: BSC 2003b, Figure 3; Viswanathan 2003, p. 23.

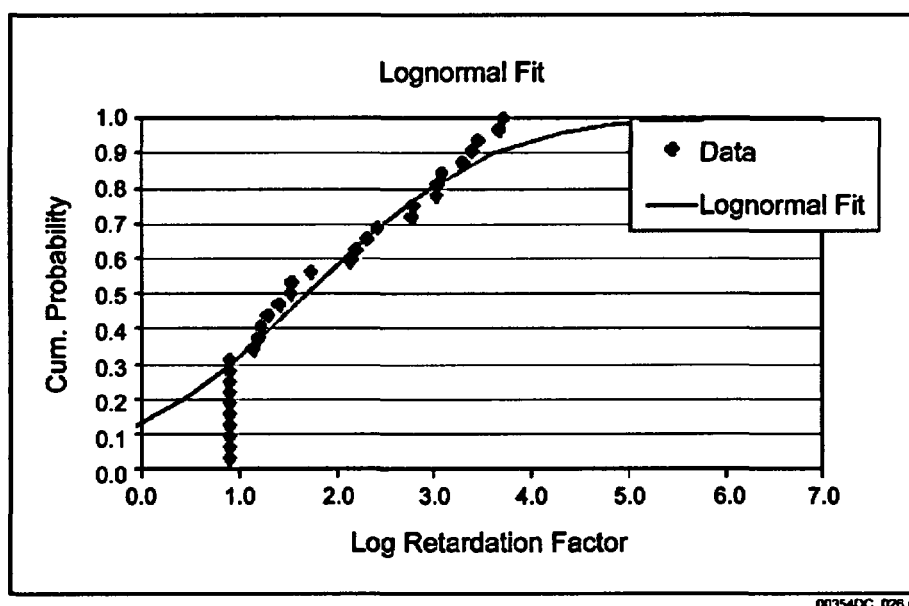
Figure 6-3. Cumulative Probability Distribution of Log Colloid Retardation Factors and a Fit to the Data for Fractured Volcanics

6.3.2.2 Colloid Transport in Alluvial Material

Background—Colloid filtration rate constants and retardation factors for alluvial material have been estimated in a number of laboratory experiments for the YMP. With the absence of YMP field data for colloid filtration in the alluvium, data from Schijven et al. (1999, Table 3, p. 1107) were used to obtain field colloid filtration and detachment rates. These laboratory column experiments have been conducted using silica and natural colloids in addition to CML microspheres. As with the fractured volcanics, colloid filtration and detachment rate constants have been derived from colloid responses in tracer tests by using the advection-dispersion equation with appropriate terms for a single reversible first-order reaction to account for mass transfer between mobile water and immobile surfaces (filtration and detachment) to fit the data.

Results: Colloid Filtration Rate Constants—Even though different sizes and types of colloids were used in the different tests, there is an apparent trend of decreasing filtration rate constant with residence time. This trend is similar to the trend witnessed in the fractured volcanics.

Results: Colloid Retardation Factors—As with the fractured volcanics, colloid retardation factors, R_{col} , can be calculated from colloid filtration and detachment rate constants. Using the interpretive results from all of the tests, a cumulative probability distribution for R_{col} was generated (Figure 6-4).



Source: BSC 2003b, Figure 5; Viswanathan 2003, p. 24.

Figure 6-4. Cumulative Probability Distribution of Log Colloidal Retardation Factors and a Fit to the Data for Alluvium Material

6.3.2.3 Fraction of Colloids Transporting With No Retardation

Several field observations have suggested that a small percentage of colloids transport with essentially no retardation in groundwater, while the majority undergoes either reversible or irreversible filtration, both of which can be modeled by a retardation factor, R_{col} .

The attachment rate constant is used to determine the fraction of the colloids that transport with no retardation. Specifically, colloids for which the ratio of the attachment rate to the travel time is greater than one will transport with no retardation. The details of determining the fraction are given in the *Saturated Zone Colloid Transport* (BSC 2003b).

6.3.2.4 Other Issues Addressed through the Testing

Validity of the Assumption That Colloid Filtration and Detachment Rates Are Fast—The use of a retardation factor to describe colloid transport through the saturated zone implicitly assumes that colloid filtration and detachment rates are fast relative to groundwater travel times through the system. This assumption is shown to be valid for at least 94 percent of the colloid mass based on distributions of filtration rate constants from laboratory and field colloid transport experiments (BSC 2003b).

Validity of Use of Microspheres—*Saturated Zone Colloid Transport* (BSC 2003b) documents laboratory experiments conducted to evaluate the applicability of CML microspheres as field-test surrogates for inorganic colloids in both saturated fractured media and saturated alluvium. The following results were obtained:

- In fracture experiments, 330-nm diameter CML microspheres consistently experienced less filtration/attenuation than 100-nm silica colloids.
- In alluvium-packed column experiments, natural colloids (most less than 100 nm) transported with slightly less filtration than 190-nm diameter CML microspheres and with considerably less filtration than 500-nm microspheres. These results suggest that (1) small (less than 200-nm diameter) CML microspheres should serve as reasonable surrogates for inorganic colloids in saturated alluvium, and (2) CML microspheres may actually serve as conservative colloid tracers in saturated fractured media (yielding transport parameter estimates that result in over prediction of inorganic colloid transport).

Validity of the Local Equilibrium Assumption for Colloids That Are Retarded—The majority fraction of colloids is retarded by the R_{col} distributions developed in this analysis. The validity of the local equilibrium assumption must be tested in order to justify the use of the R_{col} distributions. To evaluate the validity of this assumption, a simple analysis can be performed with nondimensional Damköhler numbers presented in *Saturated Zone Colloid Transport* (BSC 2003b). Bahr and Rubin (1987, p. 450) found that equilibrium was well approximated when the sum of the two Damköhler numbers is greater than 100 and reasonably well estimated when the sum is greater than 10.

For a 100-year travel time, 96 percent of the colloids will have a Damköhler number greater than 100. For a 1,000-year travel time, it will be over 98 percent; and for a 10-year travel time, it will be 94 percent. An analysis of the alluvium rate constants results in very similar results with an even greater percentage with Damköhler numbers greater than 100. Thus, the vast majority of colloids that are not part of the unretarded fraction will transport in accordance with the local equilibrium assumption.

6.4 MODEL FOR COLLOID-FACILITATED TRANSPORT FOR REVERSIBLY SORBED RADIONUCLIDES IN THE SATURATED ZONE

6.4.1 Implementation

Details of the transport model implementation are found in *Site-Scale Saturated Zone Transport* (BSC 2003a). The transport model takes the calibrated flow model (DTN: LA0304TM831231.002) described in detail in *Site-Scale Saturated Zone Flow Model* (BSC 2003e) as the starting point. Using the steady-state velocity field supplied by the flow model the downstream radionuclide concentrations are computed. Other processes that impact the transport of radionuclides that are considered include advection, dispersion, diffusion, retardation, and colloid-facilitated transport. Input parameters to the transport model are:

1. Radionuclide release locations
2. Dispersivities in the volcanics
3. Matrix porosity
4. Matrix diffusion coefficient
5. The sorption distribution coefficient K_d in the matrix
6. Flowing interval porosity
7. Flowing interval spacing
8. Retardation factor in the flowing interval
9. Effective porosity of the alluvium
10. Dispersivities in the alluvium
11. The K_d value in the alluvium.

Colloid-Facilitated Transport of Reversibly Sorbed Radionuclides—Radionuclides cannot diffuse into the matrix while attached to colloids because the colloid particles themselves cannot diffuse into the matrix (BSC 2003b). Hence, the fraction of radionuclides that are attached irreversibly onto colloids does not experience any matrix diffusion and is transported at the same rate as the colloid particles.

The fraction of colloids that are reversibly attached onto the colloids experiences a reduction in the diffusion process because this fraction can diffuse into the matrix only while unattached to the colloids. In the volcanics, this results in a reduction in the effective diffusion coefficient for the radionuclide as indicated in Equation 6-1 (BSC 2003c, Eq. 79)

$$D_e^{adjusted} = \frac{D_e}{(1 + k_c)^2} \quad (\text{Eq. 6-1})$$

where

$D_e^{adjusted}$ is the effective diffusion coefficient of the radionuclide adjusted for the effect of reversible attachment to colloids,

D_e is the effective diffusion coefficient of the radionuclide in the matrix,

k_c is the distribution parameter expressing the relative amount of radionuclide residing on the colloids with respect to that in the aqueous phase, given by (BSC 2003c, Attachment II):

$$k_c = C_c * k_{d-c} \quad (\text{Eq. 6-2})$$

where

C_c is the colloid concentration in the groundwater, and k_{d-c} is the sorption coefficient for the radionuclide onto the colloids.

In the alluvium, diffusion from the fractures into the matrix is not significant since the matrix is readily available; however, the sorption coefficient for the radionuclide onto the rock surface is modified due to the competition with the colloids as follows (BSC 2003c, Eq. 81):

$$k_d^{new} = \frac{k_d^{original}}{(1 + k_c)} \quad (\text{Eq. 6-3})$$

where

$k_d^{original}$ is the sorption coefficient for the radionuclide in the alluvium in the absence of colloids and k_d^{new} is the sorption coefficient for the radionuclide in the alluvium in the presence of reversible attachment to colloids.

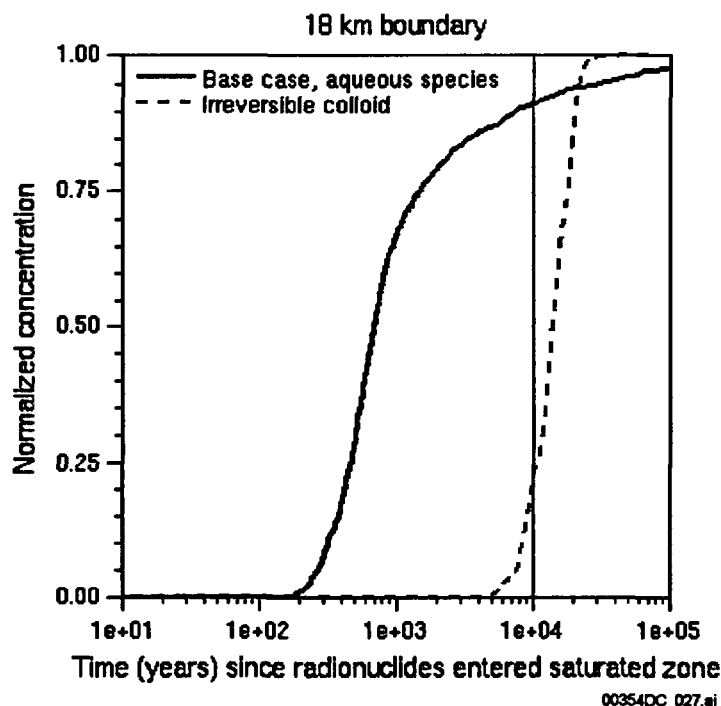
6.4.2 Model Results

Particle source locations were chosen to cover the anticipated repository footprint at the water table. Calculations were performed for an instantaneous release of particles at the source location (DTN: LA0304TM831231.002). Results presented in Figures 6-5 and 6-6 show breakthrough curves at the 18-km compliance boundary, calculated by starting 1,000 particles distributed over the repository footprint and outputting the cumulative number of particles crossing an east–west vertical plane across the entire width and depth of the model.

Calculations are presented that illustrate that the saturated-zone retards the migration of radionuclides that are bound to colloids. Given that the most deleterious colloid-related effect on saturated zone performance is likely to be the mobility of otherwise less mobile dissolved radionuclides via colloids, the focus is on that process. This analysis is restricted here to radionuclides irreversibly attached to colloids. Note that reversibly sorbed radionuclides would follow the K_c model described in Section 6.4. Furthermore, the small fraction that travels unretarded (see Section 6.3.2.3) would break through at the same time as the base case aqueous species. Therefore, the total breakthrough of a radionuclide irreversibly sorbed to the colloids would be a composite of the majority fraction colloid curve shown on the figures and the base case aqueous species that represent the small fraction of colloids that travel with no retardation.

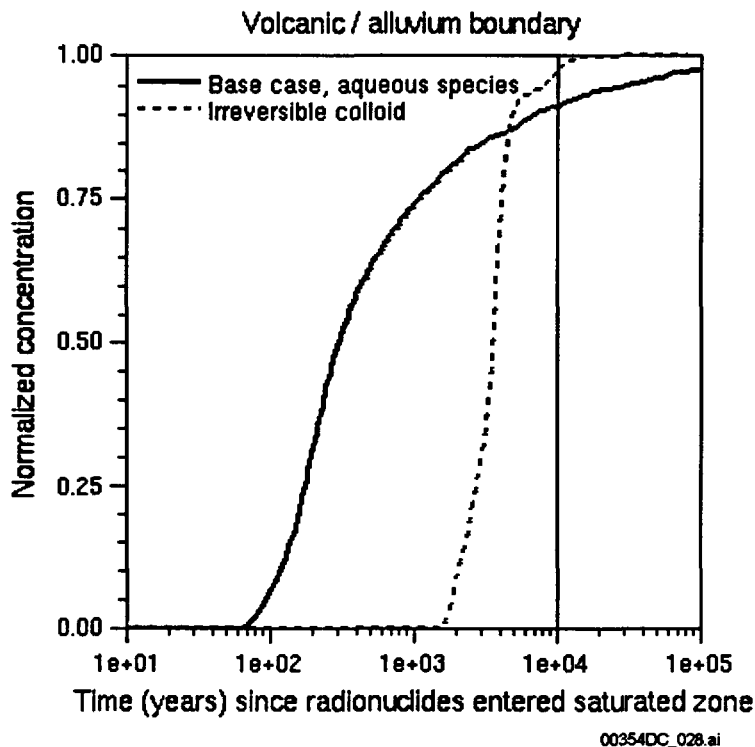
Figures 6-5 and 6-6 show the expected behavior of the majority fraction of colloidal-species transport compared to the base-case aqueous species transport. Figure 6-5 shows the

breakthrough at the 18-km compliance boundary downstream from the point at which radionuclides first enter the saturated zone. First arrivals (the base case aqueous species and the small fraction of colloids that travel unretarded) are predicted to be at about 200 years. Most of the colloid inventory (about 80 percent) that arrives at the compliance boundary, arrives after 10,000 years. Most of the aqueous species inventory (about 90 percent) arrives before 10,000 years. The majority fraction of colloids experience a significant delay in travel time. This delay is also observed at the volcanic-alluvial interface (see Figure 6-6). However, note that if larger specific discharge values were assumed, as would be the case for a future, wetter climate, the entire breakthrough curve would shift to travel times of less than 10,000 years. The technical output of the saturated zone transport model consists of breakthrough curves and travel times that will be integrated into the saturated zone model abstractions (BSC 2003c).



Source: BSC 2003a, Figure 6.7-5a.

Figure 6-5. Comparison of Breakthrough Curves for the Base Case and Radionuclides Irreversibly Attached to Colloids: 18-km Boundary



Source: BSC 2003a, Figure 6.7-5b.

Figure 6-6. Comparison of Breakthrough Curves for the Base Case and Radionuclides Irreversibly Attached to Colloids: Volcanic/Alluvium Boundary (about 18 km)

6.5 UNCERTAINTY AND SENSITIVITY

6.5.1 Data and Testing Uncertainties

Although results from field colloid transport tests and observations at several radionuclide affected field sites suggest it is reasonable to expect a small fraction of colloid mass to move unretarded through transport systems, there are uncertainties associated with the assumed partitioning of colloid mass in the saturated zone into fractions that travel unretarded and retarded. This partitioning is based largely on the assumption that the population of colloids having irreversibly-sorbed radionuclides entering the saturated zone has a cumulative distribution of filtration rate constants approximately equal to the cumulative distribution of filtration rate constants observed in laboratory and field saturated zone colloid transport experiments. Although the colloids generated in the engineered barrier system will have some characteristics different from the colloids used in the saturated zone transport experiments, the overall transport behavior of the colloids is not expected to differ significantly.

Additional uncertainty is introduced as a result of extrapolating the cumulative distribution of observed filtration rate constants to very low probabilities for the purposes of estimating colloid mass fractions that move unretarded. In part to address these unquantifiable uncertainties, the distributions of filtration rate constants in the volcanics and alluvium are combined to obtain a single filtration-rate constant distribution to estimate colloid mass fractions that move unretarded through the entire saturated zone.

Uncertainties are also associated with the retardation factors obtained for both the volcanics and alluvium:

1. All the laboratory and field transport data used to derive the distributions were obtained at scales much smaller than the scales of interest for TSPA modeling.
2. The retardation factors derived from many of the transport tests were based on fitting the low colloid concentrations in the tails of breakthrough curves. These tails were sometimes barely above detection or quantification limits, resulting in the fitted retardation with potentially considerable uncertainty. However, long tails are virtually always observed whenever analytical methods are sensitive enough to capture them.

These uncertainties are addressed by:

1. Assigning lower bounds for retardation factors to cumulative distributions in the volcanics and alluvium such that significant retardation of colloids always occurs, and
2. Assuming that a small fraction of colloid mass moves unretarded through the transport system.

The two sets of laboratory alluvium colloid transport experiments yielded significantly different results for both CML microsphere and inorganic colloid transport in alluvium (BSC 2003b). These disparate results, though possibly explainable by the presence of air bubbles in one set of experiments, can be interpreted as imparting potential uncertainty to colloid transport in alluvium. This uncertainty is preserved by including both sets of experimental results in the overall data set used to develop the cumulative distributions for colloid-filtration-rate constants and retardation factors in alluvium, resulting in the distributions of Figures 6-3 and 6-4.

6.6 MODEL CONFIDENCE BUILDING

6.6.1 Model Validation

Recognizing that the site-scale saturated zone transport model is being used to perform probabilistic calculations in which parameter uncertainties are propagated through the model, the intent of validation was to confirm the appropriateness of the radionuclide parameters and processes included in the model. Confidence in the results of the model was built by a series of different approaches that included: (1) comparisons to analog sites, (2) model-data comparisons, (3) comparison with data published in refereed journals, and (4) comparison to an independent site-scale groundwater flow model for the Yucca Mountain saturated zone.

The data used in the confidence building for the relevant transport parameters (e.g., sorption coefficient), submodel processes (e.g., advection, sorption), and site scale model processes (e.g., flow pathways, transit times) were based on laboratory testing, field tests, natural analog sites, and expert elicitations. The model was validated by post development comparison of model transit times with those inferred from carbon-14 data and qualitative comparison of flow paths predicted by the model and those inferred from the hydrochemistry data.

6.6.2 Alternate Models

An alternative conceptual model was considered to evaluate colloid transport in the saturated zone transport. These evaluations are summarized in Table 6-1.

Table 6-1. Alternative Conceptual Models Considered

Alternative Conceptual Model	Key Assumptions	Screening Assessment	Basis
Locally varying transport properties	Transport properties are strong functions of local water chemistry, rock mineralogy, and solute concentrations. The properties have to be calculated locally at each node along the travel path.	This alternative conceptual model is implicitly included in the saturated zone transport model through the range of uncertainty in the sorption-coefficient values.	<p>The approach taken in this model report is to use linear transport equations with transport parameters appearing in the equations being treated as "effective" stochastic variables appropriate for the model scale. This approach is consistent with the current level of available data. Transport parameters such as the K_d coefficients depend on type and concentration of the species, rock mineralogy, and groundwater pH and Eh. In the present model, broad distributions have been developed for effective K_ds (BSC 2003a, Attachments I, II, and III). No credit is being taken for sorption onto zeolites, and the K_d distributions presented in Attachment I are based on silica surfaces. Given the current level of data availability, water pH data are being treated as spatially random along the transport path, and oxidizing conditions are taken as a conservative assumption, as justified in Section 5 of this report.</p> <p>To evaluate the effect of scale on the K_d distributions, calculations were performed to capture the effect of spatial variability of rock types and variability in water chemistries on effective K_d (BSC 2003a, Attachment II). The effect of variability in water chemistry was captured in the input K_d distributions that were used for effective K_d calculations. It was observed that the effective K_d distributions calculated for a single 500-m-by-500-m grid block were narrower than the input K_d distributions. During performance assessment modeling studies, calculations will be made through multiple runs, each with a distinct K_d value sampled from the above-mentioned effective K_d distribution. This approach will be more approximate than assigning K_d values on a node basis, as the latter approach will lead to breakthrough behavior that can be described by an even narrower distribution than the effective K_d distribution.</p>

Source: BSC 2003a, Table 6.4-1.

6.7 SUMMARY OF SATURATED ZONE SCREENING ARGUMENTS

Field experiments using fluorescent CML microspheres and laboratory experiments using both natural colloids and the CML microspheres show that the longer the colloids travel through the fractured volcanics, the higher the probability that they will be reversibly or irreversibly filtered by the immobile rock phase. These results support the assumption that most colloids are filtered early on and that only a small percentage remain unretarded.

Laboratory experiments for alluvial materials pertaining to Yucca Mountain using both natural colloids and CML microspheres suggest that colloid filtration decreases with time. Several of the field observations for alluvial materials have suggested that the majority of the colloids undergo reversible or irreversible filtration and only a small percentage of the colloids move unretarded.

Sensitivity analyses performed comparing the travel time through the fracture volcanics in the saturated zone of aqueous radionuclides and of colloids with irreversibly attached radionuclides show that the colloid releases lag considerably behind the release of the aqueous species. The analyses suggest that, if radioactive colloids reach the saturated zone within the regulatory compliance period of 10,000 years, the saturated zone can significantly retard their release to the accessible environment. Some radioactive colloids could be released to the biosphere within 10,000 years but that is likely to be a small fraction of the total radioactive colloid concentration entering the saturated zone.

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7. SUMMARY

The presence of colloids at the Yucca Mountain site raises the potential of accelerating the transport of radionuclides from the repository to a natural or man-made discharge point at the biosphere. There are several potential sources of colloids in groundwater (e.g., clay minerals, metal oxides, viruses, bacteria and humic macromolecules). It has been suggested that dissolved groundwater contaminants could have high affinity to sorption onto the surfaces of suspended colloids. As a result, colloids could possibly act as carriers for contaminants in natural subsurface environments and be significant contributors to the rate of migration of radionuclides. However, for colloids to provide a significant means for the transport of radionuclides from the waste form to the biosphere and, consequently, be a major contributor to dose, colloidal suspensions must:

1. Contain high enough concentrations of colloids to carry a significant mass of radionuclides relative to the mass of dissolved radionuclides
2. Be stable for distances on the order of tens of kilometers and for time periods of tens of thousands of years
3. Not appreciably attach to immobile rock surfaces.

If one or more of these conditions are not met, the importance of colloid-facilitated transport to system performance significantly decreases.

In order to assess the overall significance of colloid transport to system performance, the formation, stability, transport and filtration of colloids were examined for the waste package, the invert, the unsaturated zone and the saturated zone. The most important phenomena affecting colloids in each of those subsystems were identified and examined to reach risk-informed screening arguments. Those screening arguments are summarized in the sections that follow. Their cumulative qualitative effect on the release of radioactive colloids to the biosphere was presented in Figure 1-2. This assessment leads to the conclusion that colloid-facilitated radionuclide transport is not as important to system performance as transport of radionuclides as dissolved species.

7.1 COLLOID FORMATION, STABILITY, AND TRANSPORT IN REPOSITORY SUBSYSTEMS

7.1.1 Waste Package

Three different types of colloids are considered in the modeling of the radionuclide source term:

1. Waste-form colloids resulting from corrosion of defense high-level radioactive waste glass are primarily smectite colloids with embedded discrete phases of plutonium and americium;
2. Iron oxyhydroxide colloids resulting from the corrosion of waste package and metallic invert materials; and

3. Natural colloids in groundwater and seepage water.

Concerning the third type, humic substances are not considered to be sufficiently abundant in Yucca Mountain groundwater to be of significant impact to radionuclide transport. Also, microbes, due to their relatively large size ($\sim 1 \mu\text{m}$) within the colloid-size range, are highly susceptible to filtration. Therefore, natural colloids at the Yucca Mountain site are modeled as smectite colloids.

True or intrinsic colloids were eliminated from consideration in TSPA analyses for two reasons. First, long-term corrosion testing with CSNF and DSNF under unsaturated, oxidizing conditions have produced very low colloid concentrations and small amounts of uranium within the colloid mass. Second, the same test indicates that meta-schoepite and UO_{2+x} colloids readily dissolve upon the introduction of J-13 groundwater.

Except for the amounts of plutonium and americium that can be (1) irreversibly embedded within defense high-level radioactive waste glass colloids, and (2) irreversibly sorbed to iron oxyhydroxide colloids, it is assumed that radioactive colloids are formed by the reversible sorption of dissolved radionuclides onto smectite colloids under equilibrium conditions and can be described by a distribution coefficient. The reversible sorption of plutonium, americium, protactinium, thorium, and cesium onto colloids is modeled using K_d values, the mass of dissolved radionuclides and the colloid concentration.

The stability of colloid suspensions within the waste package and the drift will be highly dependent on the evolution of the physical and chemical conditions. For example, relative humidity decreases to low values shortly after emplacement of the waste containers. With time, as the containers cool down, the relative humidity increases asymptotically to 100 percent after about 2,000 years. At lower relative humidity, the groundwater entering the drift concentrates due to water evaporation and this, in turn, would lead to a high-ionic-strength solution. Colloid suspensions are not stable at ionic strengths above 0.05 M. Therefore, stable colloid suspensions during the first 2,000 to 3,000 years after repository closure are not likely.

Only diffusive releases typically occur for the nominal case, and thus colloid transport is minor over the regulatory 10,000-year period. Advective releases from seeping water can potentially occur for containers disrupted by the seismic scenario or the volcanic scenario.

The seepage-water dripping scenario is the most relevant in-package chemistry scenario with regard to colloid transport. For this scenario, reaction-path calculations indicate that the initial seepage water composition is rapidly overtaken by water-package interactions. Depending on the seepage flux the water can reach an ionic strength higher than 0.05 M, the lower ionic-strength limit for stable colloid suspension. Therefore, under the relevant in-package chemistry scenario, it is unlikely that colloid suspensions will be stable. Furthermore, once formed and stably suspended, colloids could be filtered within fractures in fuel pellets or trapped at the boundaries of disaggregating grains. Notwithstanding these potential colloid filtration processes that would reduce the amount of radioactive colloids released from the waste package, it has been assumed that the waste package does not provide a barrier to the release of radioactive colloids.

7.1.2 Invert

The drift invert beneath the waste packages, which is primarily composed of crushed tuff rocks, will likely be in intimate contact with the waste package. In the nominal scenario the invert would limit advective transport of radionuclides out of the engineered barrier by maintaining unsaturated conditions under the waste package.

The invert is expected to act as a mixing cell. Any seepage water entering the invert would combine with the water flowing from a damaged waste package, possibly altering the chemistry of the water from the waste package. Any incoming water would usually be overwhelmed by the reaction with the invert material, and the resulting solution would usually be similar to J-13 groundwater with a neutral to slightly basic pH. As a result, any iron oxyhydroxide colloids may become unstable. Also, the evaporation process may concentrate the solution, which may further increase the instability of colloids in the invert.

The corrosion of invert support will generate iron and copper oxides, which are generally strong adsorbents for various radionuclides. Corrosion products would tend to be localized and relatively far apart from each other, with the possibility that seepage water from the waste package could completely miss corrosion products in the invert. There is a low probability that radionuclides will come into contact with corrosion products. Therefore, the sorption effect of these corrosion products is not considered in the current TSPA calculations.

The extent of colloidal filtration within the invert is not expected to be significant due to the short filtration path.

7.1.3 Unsaturated Zone

Most colloid transport studies have been under saturated conditions; hence, much of the information related to colloid transport in unsaturated media has been inferred from such studies, augmented by information available from the limited experimental studies under unsaturated conditions. The current state of understanding regarding colloids in groundwater native to the Yucca Mountain site is that natural colloids are present in low concentrations and the preponderance of colloids affecting radionuclide transport will be waste-form colloids.

Colloid transport through the unsaturated zone at Yucca Mountain is expected to be primarily through fractures because of pore-exclusion effects. The extremely small pores in some of the geologic formations within the unsaturated zone will likely provide a barrier to colloid transport. This is particularly important because large contrasts in porosity between adjacent formations have been shown to increase colloid filtration.

The effect of the air-water interface on colloid transport is determined by the affinity of colloids to attach to the interface and the degree of saturation. Based on the current understanding, it is concluded that the attachment of colloids to the air-water interface will be to retard colloid transport.

Pseudocolloids, with radionuclides either reversibly or irreversibly adsorbed, are the only radioactive colloids that are considered to be transported through the unsaturated zone below the

repository, except for waste form colloids derived from defense high-level radioactive waste glass.

7.1.4 Saturated Zone

Colloids carrying radionuclides are assumed to enter the saturated zone due to downward travel through the fractures in the unsaturated zone directly below the repository foot print. Once they have entered the saturated zone, colloids will travel preferentially along horizontal paths until they reach the biosphere through a natural or man-made discharge point.

Colloid filtration rate constants and retardation factors for colloid transport in fractured volcanics have been estimated from a number of laboratory and field experiments. These experiments suggest that the longer the colloids have to travel through the saturated medium, the higher the probability that they will be reversibly or irreversibly filtered by the immobile rock phase. These results support the assumption that most colloids are filtered early on and that only a small percentage remain unretarded.

Colloid filtration rate constants and retardation factors for alluvial materials pertaining to Yucca Mountain have been estimated from laboratory tests. As with experiments in fractured volcanics, colloid-related parameters were obtained by fitting the solution of the advection-dispersion equation with a reversible linear model for mass transfer between the mobile and immobile rock to tracer tests. Several of the field observations have suggested that the majority of the colloids undergo reversible or irreversible filtration, captured with a retardation factor, and only a small percentage of the colloids move unretarded.

Analyses performed to test the validity of the linear equilibrium-based adsorption model used to account for colloid retardation suggest that the equilibrium retardation factor for colloids is valid for the vast majority of colloids that get retarded.

Sensitivity analyses performed comparing the travel time through the fractured volcanics in the saturated zone of dissolved radionuclides and of colloids with irreversibly attached radionuclides show that the colloid releases lag considerably behind the release of the dissolved species. The analyses show that, if radioactive colloids reach the saturated zone within the regulatory period of 10,000 years, the saturated zone can significantly retard their release to the biosphere. Some radioactive colloids could be released to the biosphere within 10,000 years but that is estimated to be a small fraction of the total radioactive colloid concentration entering the saturated zone.

7.2 CONCLUDING REMARKS

The conclusion of this technical basis document is that the contribution to system performance due to radionuclides carried by colloids from the waste form to the biosphere is insignificant. Some radionuclides (e.g., plutonium and americium) may reach the biosphere primarily in colloidal form, but in insignificant amounts compared to amounts of other radionuclides that arrive primarily as dissolved species, such as technetium, iodine, and neptunium.

Different phenomena act upon colloids in their migration from the waste form to the biosphere. These phenomena lead to a continuous decrease in the concentration of colloids as they travel from one repository subsystem to the next. It has been shown that colloidal suspensions in the

drift and the perturbed near-field environments are unlikely to be sufficiently stable due to thermal-chemical conditions, such as high temperature and high ionic strengths. Analyses of experimental data have shown that, under the perturbed conditions expected at the Yucca Mountain site, the probability that colloids will be present in high enough concentrations to effectively compete with the immobile rock for the adsorption of dissolved radionuclides is unlikely.

In addition, large physical changes in the porosity of hydrologic units in the unsaturated zone below the repository, causing the flow to suddenly change from preferentially fracture flow to matrix flow, effectively retards or even prevents colloid transport. When such changes occur between hydrologic units, the interface between the units acts as a very effective colloid filter. The net effect of the changes in the porosity of hydrologic units in the unsaturated zone is considerable reduction in (1) colloid concentrations and (2) mass of radionuclides being carried by colloids; thus, the source of radioactive colloids into the saturated zone is reduced.

Colloid-facilitated transport of radionuclides is further attenuated in saturated zone leading to the conclusion that colloid-facilitated transport of radionuclides is not a significant contributor to system performance. This low importance leads to the corollary that the uncertainties in colloid-transport-related phenomena and parameters are not important to the uncertainty in the system performance. Therefore, these phenomena and parameters would not appear as important in the uncertainty/sensitivity analyses based on total system performance.

The discussion in this technical basis document comprises a risk-based screening argument for colloid-facilitated transport of radionuclides. However, it is not suggested that colloid-facilitated transport be excluded from the TSPA. Rather, it is concluded that on a risk basis, colloid-facilitated transport is not a significant contributor to estimating system performance, and therefore, issues associated with this transport mode are of relatively low importance. It is also concluded that the current modeling approach for colloid-facilitated transport of radionuclides in TSPA is adequate for its purpose.

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APPENDIX A

**EXCLUSION OF ENTRAINED COLLOIDS
IN THERMAL-CHEMICAL ALTERATION
(RESPONSE TO ENFE 1.06, ENFE 4.04, AND GEN 1.01 (COMMENT 35))**

Note Regarding the Status of Supporting Technical Information

This document was prepared using the most current information available at the time of its development. This Technical Basis Document and its appendices providing Key Technical Issue Agreement responses that were prepared using preliminary or draft information reflect the status of the Yucca Mountain Project's scientific and design basis at the time of submittal. In some cases this involved the use of draft Analysis and Model Reports (AMRs) and other draft references whose contents may change with time. Information that evolves through subsequent revisions of the AMRs and other references will be reflected in the License Application (LA) as the approved analyses of record at the time of LA submittal. Consequently, the Project will not routinely update either this Technical Basis Document or its Key Technical Issue Agreement appendices to reflect changes in the supporting references prior to submittal of the LA.