

**STATUS OF COLLOID RELEASE EVALUATIONS
—LETTER REPORT**

Prepared for

**U.S. Nuclear Regulatory Commission
Contract NRC-02-07-006**

Prepared by

H. Basagaoglu

**Center for Nuclear Waste Regulatory Analyses
San Antonio, Texas**

July 2008

ABSTRACT

Colloid-facilitated radionuclide transport may affect radionuclide release and subsequent transport at the potential Yucca Mountain repository site if the geochemical and hydrogeological conditions sustain stable colloidal suspensions at sufficient mass concentrations during the postclosure period. In the absence of mobile colloids in the repository environment, kinetically reversibly sorbing radionuclides (e.g., plutonium and americium) could attach to stationary corrosion products, and hence their releases and transport could be delayed and their peak release rates could decrease. However, radionuclides irreversibly and reversibly attached to mobile colloids could be transported faster than the average groundwater velocity in fractured flow domains and hence could result in earlier releases to the accessible environment.

This status report summarizes our current understanding of the U.S. Department of Energy abstraction implemented in the Total System Performance Assessment–License Application model for the colloid-facilitated radionuclide transport in the in-package environment and the engineered barrier system. The status report specifically focuses on (i) type, mass concentrations, and stability of colloidal suspension; (ii) underlying assumptions of the abstraction and the relevant features, events, and processes; and (iii) importance of irreversible and reversible colloid types to radionuclide transport.

CONTENTS

Section	Page
ABSTRACT	ii
FIGURES	iv
TABLES	iv
ACKNOWLEDGMENTS	v
1 INTRODUCTION	1
1.1 Colloid Transport Abstraction	1
1.2 Features, Events, and Processes.....	2
1.3 Major Assumptions in the DOE Abstraction	3
1.4 Risk Insights and Potential Effects on Repository Performance	4
2 ABSTRACTION	5
2.1 Colloid Sources	5
2.2 Representative Colloids.....	6
2.3 Stability of Colloids	8
2.4 Mass Concentration of Colloids.....	10
2.4.1 Smectite (DHLWG) Colloids	10
2.4.2 Iron Oxyhydroxide Colloids.....	11
2.4.3 Zirconium Oxide Colloids.....	11
2.4.4 Uranophane Colloids	11
2.4.5 Smectite (Groundwater) Colloids.....	11
2.5 Sorption/Desorption of Radionuclides Onto Colloids.....	12
2.5.1 Irreversible Sorption.....	12
2.5.2 Reversible Sorption	13
2.5.3 Reversible Competitive Sorption (Sorption Capacity Model).....	13
2.5.4 Sorption Distribution Coefficients K_d and K_c	14
2.6 Sorption/Desorption of Radionuclides Onto Immobile Corrosion Products	15
2.7 Radionuclide Mass Concentrations Associated With Irreversible Colloids.....	15
2.7.1 Smectite Colloids Associated With DHLWG	15
2.7.2 Iron Oxyhydroxide Colloids.....	15
2.7.3 Zirconium Oxide Colloids.....	15
2.8 Radionuclide Mass Concentrations Associated With Reversible Colloids	16
2.8.1 Smectite (DHLWG) Colloids	16
2.8.2 Iron Oxyhydroxide Colloids.....	16
2.8.3 Uranophane Colloids	16
2.8.4 Smectite (Groundwater) Colloids.....	16
2.9 Alternative Models.....	16
2.9.1 Two-Site Kinetic Model	16
2.9.2 Rate of Colloid Generation Model.....	17
2.9.3 Mechanisms of Colloid Generation.....	17
2.10 Uncertainties.....	17
3 SUMMARY.....	17
4 REFERENCES	18

FIGURE

Figure	Page
2-1 A Schematic Representation of Radionuclides Reversibly or Irreversibly Associated (or Sorbed Onto) Different Colloid Types and Stationary Corrosion Products	7

TABLE

Table	Page
2-1 Radionuclides Reversibly or Irreversibly Associated With (or Sorbed Onto) Different Colloid Types and Stationary Corrosion Products	8

ACKNOWLEDGMENTS

This report was prepared to document work performed by the Center for Nuclear Waste Regulatory Analyses (CNWRA) and its contractors for the U.S. Nuclear Regulatory Commission (NRC) under Contract No. NRC-02-07-006. The activities reported here were performed on behalf of the NRC Office of Nuclear Material Safety and Safeguards, Division of High-Level Waste Repository Safety. The report is an independent product of CNWRA and does not necessarily reflect the views or regulatory position of NRC.

The author wishes to thank P. Bertetti for a thorough technical review, G. Wittmeyer for programmatic review, and L. Mulverhill for editorial comments and improvements to the manuscript. Appreciation also is extended to L. Naukam for assistance in preparation of the report.

QUALITY OF DATA, ANALYSES, AND CODE DEVELOPMENT

DATA: All CNWRA-generated data contained in this report meet quality assurance requirements described in the Geosciences and Engineering Division Quality Assurance Manual. Sources of other data should be consulted for determining the level of quality of those data.

ANALYSES AND CODES: No codes were used in the analyses contained in this report.

1 INTRODUCTION

Colloid-facilitated radionuclide transport may affect radionuclide releases and subsequent transport at the potential Yucca Mountain repository site during the postclosure period if the colloidal suspensions, at sufficient mass concentrations, remain stable and migrate in fast flow paths. Colloid-associated radionuclides may have shorter residence times than dissolved radionuclides in a flow domain, and hence colloid-facilitated radionuclides may result in higher concentrations in an accessible environment than dissolved radionuclides. Irreversibly sorbing radionuclides (plutonium and americium) could migrate faster than their dissolved counterparts if they attach onto mobile colloids; otherwise, they may alternatively sorb kinetically onto stationary surfaces, and hence their releases and transport could be delayed. Thus, the presence of reversible and irreversible colloids in the flow domain may both increase radionuclide releases and facilitate their subsequent transport.

At the potential Yucca Mountain repository site, wasteform colloids [defense high-level waste glass (DHLWG)¹ and spent nuclear fuels (SNF)²], steel corrosion product colloids, and groundwater colloids are expected to exist. Radionuclides could be irreversibly embedded in certain types of colloids or could reversibly or irreversibly sorb onto some other types of colloids. The fate and transport of radionuclides irreversibly embedded in or sorbed onto colloids are determined by the fate and transport of the suspended colloids on which they are carried. Irreversibly sorbed or embedded colloids could be physically filtered, or the chemical conditions could make the suspension unstable in the engineered or natural barrier systems. As a result, radionuclides associated with these colloids may not be transported. On the other hand, reversibly sorbed radionuclides could potentially go back into solution (when the solution is below the solubility limit) even if the suspended colloids they sorb onto are filtered or become unstable. Both irreversible and reversible colloids could potentially enhance the radionuclide transport at the Yucca Mountain site, depending on the geochemical conditions and flow rate.

1.1 Colloid Transport Abstraction

The main purpose of the U.S. Department of Energy (DOE) Colloid Abstraction (Sandia National Laboratory, 2007a) model is to estimate the stability and mass concentration of colloid suspensions and mass concentrations of radionuclides associated with the colloids in the in-package and engineered barrier system (EBS)³ components during the postclosure period. The stability and mass concentration of suspensions are based on in-package and in-drift fluid chemistry and in-package dissolved radionuclide concentrations. The abstraction addresses the reversible and irreversible association of radionuclides with mobile colloidal particles and immobile corrosion products, and colloid-facilitated and dissolved radionuclide transport in the in-package environment and EBS. In the abstraction, from the modeling standpoint, irreversible sorption of radionuclides onto and irreversible embedding of radionuclides into mobile colloids are numerically treated the same.

¹Defense high-level waste glass is referenced frequently throughout this report; consequently, the acronym DHLWG will be used.

²Spent nuclear fuels is referenced frequently throughout this report; consequently, the acronym SNF will be used.

³Engineered barrier system is referenced frequently throughout this report; consequently, the acronym EBS will be used.

Specific parameters developed by process-level simulations and experimental analyses for use in the abstraction for the Total System Performance Assessment–License Application (TSPA–LA)⁴ model include

- Ionic strength and pH of in-package and in-drift (invert) fluids
- Empirical probability distributions for colloid masses produced by degradation of wasteforms and corrosion of EBS components
- Radionuclide mass concentrations generated from wasteform degradation
- Sorption distribution coefficients for radionuclides that sorb on mineral phases and colloids
- Rate of irreversible attachment of only plutonium and americium onto corrosion product colloids
- Range of specific surface areas and surface site densities for smectite clay, uranophane, and iron oxyhydroxide

Feeds for in-package ionic strength and pH are from Sandia National Laboratory (2007b), feeds for in-drift ionic strength and pH are from Sandia National Laboratory (2007c), and feeds for dissolved radionuclide concentrations are from Sandia National Laboratory (2007d). The other input parameters for the abstraction are discussed in the subsequent sections.

In the DOE abstraction, colloid transport is unimpeded in the invert. However, based on the ionic strength and pH of the seepage water in the invert, the model redistributes the reversibly sorbed radionuclides and dissolved radionuclides based on the sorption distribution coefficients of radionuclides and the total mass of colloids present in the system. The irreversibly sorbed radionuclides are not redistributed in the invert. Hence, major output quantities from the wasteform and EBS colloid abstraction to the unsaturated zone include

- DHLWG, SNF, and corrosion product colloid concentrations and groundwater colloid masses
- Irreversibly and reversibly sorbed radionuclide masses on the mobile colloids and immobile corrosion products

1.2 Features, Events, and Processes

Features, events, and processes are related to the formation of wasteform, corrosion products, and groundwater colloids and their suspension stability in the EBS. The following features, events, and processes are included in the DOE abstraction

- Chemical interaction with corrosion products
- Formation of pseudocolloids (groundwater or seepage) in the EBS

⁴Total System Performance Assessment–License Application is referenced frequently throughout this report; consequently, the acronym TSPA–LA will be used.

- Formation of corrosion product colloids in the EBS
- Stability of colloid suspensions in the EBS
- Formation of wasteform colloids by co-precipitation in the EBS

The following features, events, and processes are excluded in the DOE abstraction.

- Formation of true (intrinsic) colloids in the EBS (DOE noted that they are usually not stable and dissolve into the aqueous solution as they migrate or sorb onto groundwater or iron oxyhydroxide colloids).
- Formation of microbial colloids in the EBS (DOE noted that humic substances are not sufficiently abundant in the Yucca Mountain environment).
- Filtration of colloids in the EBS (DOE considered neglecting physical filtering to be bounding).
- Transport of particles larger than colloids in the EBS. {The size of colloids typically ranges from 1 nm to 1 μm [3.9×10^{-8} to 3.9×10^{-5} in]. In the abstraction, the size of colloids is confined to 50 to 300 nm [19.7×10^{-7} to 118.1×10^{-7} in] and is sampled from a uniform distribution. DOE noted that larger particles, if they form, are assumed to settle by gravity within a small distance, and hence their transport by moving water would be insignificant}.
- Colloid sorption at the air–water interface. (There is no specific data relevant to the Yucca Mountain site. DOE considered neglecting this process to be conservative, because colloid-facilitated radionuclide releases would be lower if colloid sorption at the air–water interface was included in the TSPA–LA model.)
- Gravitational settling of colloids in the EBS (DOE considered neglecting this process to be bounding).

1.3 Major Assumptions in the DOE Abstraction

- The sorption distribution coefficients, K_d , for thorium and protactinium were assumed to be the same as those of americium for all colloid types because of limited relevant data. DOE noted that this assumption was bounding within the range of pH of interest at the Yucca Mountain site.
- Wasteform colloidal suspensions produced at 90 °C [194 °F] would be stable at 25 °C [77 °F]. Particles would have higher chances for collisions (that may lead to flocculation) at high temperatures than at low temperatures, which would make colloidal suspension less stable. Thus, colloid suspensions stable at high temperatures would likely be also stable at low temperatures.
- Wasteform colloid particles were assigned a specific diameter for application of Derjaguin-Landau-Verwey-Overbeek theory in the model, which requires a single particle size in calculations. Based on Sandia National Laboratory (2007e), the particle size ranged from 30 to 300 nm [10×10^{-7} to 100×10^{-7} in] and is sampled from a uniform

distribution. The sampled particle size is used to calculate the diffusion coefficient of a particle.

- Plutonium and americium were considered to be associated irreversibly (embedded) or reversibly with DHLWG colloids.
- Irreversible colloids from SNF were described as ZrO_2 particles. Irreversible association of plutonium and americium with ZrO_2 was based on experimental findings. DOE noted that the choice of ZrO_2 was based on the availability of surface charge data that could be put into an effective model.
- DOE assumed that colloid meta-autunite (a layered uranyl phosphate) was a reasonable analog for a uranophane colloid. The assumption that reversible uranophane colloidal suspension could be related to meta-autunite colloid behavior was supported by experimental observations and analysis of various uranium phases.
- Colloids derived from the corrosion of waste-package materials could be represented as hematite for stability calculations. This assumption was supported by experimental observations and analyses of corroded stainless steels.
- Colloid sorption at the air–water interface was not considered in the abstraction. DOE noted that this assumption was conservative. Moreover, DOE noted that modeling of the air–water attachment process without specific, relevant repository data would be speculative.

1.4 Risk Insights and Potential Effects on Repository Performance

Mobile irreversible colloids could enhance radionuclide transport if they are generated at sufficient mass concentrations and remain stable in the waste package, EBS, and unsaturated zone environments. Stable colloidal suspensions could experience less retardation and travel faster than the average water velocity or inert tracers. This could lead to faster transport of radionuclides as they sorb onto mobile colloids that migrate preferentially in high flow paths (size exclusion effects) as compared to dissolved radionuclides. Fast flow paths could result in early arrival of radionuclides to accessible environments at high concentrations. Moreover, kinetically reversibly sorbing radionuclides could sorb onto stationary corrosion products if geochemical and hydrological conditions do not sustain stable colloidal suspensions in the flow domain. This could lead to delays in releases and subsequent transport of highly sorbing radionuclides. The removal amount and rate will be limited by available sites on the surface of stationary corrosion products for kinetic sorption.

DOE staff predicted that smectite colloids of DHLWG were highly stable under in-package chemistry conditions and in groundwater from the Yucca Mountain environment (Sandia National Laboratory, 2007a). The DOE staff also considered that Commercial Spent Nuclear Fuel (CSNF)⁵ plutonium colloids may persist for a million years if CSNF is present and undergoes degradation and the solution conditions are suitable for stable colloidal suspensions.

⁵Commercial Spent Nuclear Fuel is referenced frequently throughout this report; consequently, the acronym CSNF will be used.

DOE further noted that the effect of uranophane colloids on radionuclide transport would be unimportant, because the sorption distribution coefficient (K_d) for plutonium and americium (thorium and protactinium) onto uranophane colloids is much smaller than onto smectite and iron oxyhydroxide colloids. DOE considered that uranophane colloids are also less important for neptunium, tin, radium, and cesium transport (Sandia National Laboratory, 2007a). However, irreversible association of plutonium and americium with ZrO_2 could be potentially significant. Similarly, irreversible attachment of plutonium and americium onto iron oxyhydroxide colloids may facilitate their transport.

Briefly, among all colloid types, DOE considered uranophane colloids to be the least significant for radionuclide transport and repository performance. The most significant colloidal suspensions are largely determined by their mass concentrations, stability, and the availability of radionuclides under transient geochemical conditions.

DOE used the product of the radionuclide sorption distribution coefficient and the mass concentration of a colloid type to determine the level of risk significance of reversibly attached radionuclides (this product is represented by parameter K_c in Section 2.5.4). If the distribution of K_c for a particular radionuclide–colloid pair has a significant probability (i.e., above about 10 percent of the cumulative probability) for K_c values greater than 0.1, DOE considered that particular colloid type will facilitate the transport of a particular radionuclide. Using this criterion, DOE estimated that smectite colloids, for example, could have a significant role in tin transport in the EBS (Sandia National Laboratory, 2007a).

2 ABSTRACTION

2.1 Colloid Sources

In the DOE abstraction, the following natural and man-made components and processes were considered sources for radionuclide-associated colloids.

- Degradation of the wasteforms including DHLWG, CSNF, and Defense Spent Nuclear Fuel (DSNF)⁶
- Corrosion products from the steel components of the repository
- Natural groundwater colloids near Yucca Mountain

Immersion corrosion test results were used to obtain the range and/or empirical distributions for the colloid mass concentrations derived from DHLWG, CSNF, and DSNF (Section 2.4), which were used as an input to the abstraction. DOE conducted model validation for DHLWG and CSNF colloids (Sandia National Laboratory, 2007a,e).

⁶Defense Spent Nuclear Fuel is referenced frequently throughout this report; consequently, the acronym DSNF will be used.

In the DOE abstraction, the colloid source term is defined as the total mass of radionuclides associated with colloids that mobilize at the surface of wasteform, transport within the waste package to the waste package wall, leave the waste package through holes in the waste package wall, and enter the drift.

2.2 Representative Colloids

In the DOE abstraction, four primary particles were chosen to represent the major colloid types that may contribute to colloid-facilitated radionuclide transport in the waste package and in-drift environment:

- Smectite clay colloids—Derived from degradation of DHLWG and smectite-type clay formed from silicate tuff rock. The representative colloid in the abstraction is montmorillonite smectite. The choice of montmorillonite was based on its high specific surface area relative to other smectite phases, which makes it a dominant radionuclide-bearing colloid under groundwater conditions.
- Iron oxyhydroxide colloids—Derived from corrosion of EBS steel components (carbon-steel and stainless-steel weathering products). DOE used hematite as the representative colloid in the abstraction (Sandia National Laboratory, 2007a,e).
- Zirconium oxide colloids—Form on the surface of corroded CSNF. Because of limited available data, ZrO_2 was chosen to be the representative model colloid.
- Uranophane colloids—Form from SNF. Meta-autunite was used as a substitute for uranophane.

These colloid types were selected based on the evaluation of likely long-term alteration of the wasteforms and waste-package materials and the secondary phases most capable of forming viable colloids. However, DOE acknowledged that specific physical data on these particles are lacking. In the DOE abstraction, these colloids are different in their (i) mass concentrations, (ii) ionic strength and pH-dependent stability criteria, (iii) available sorption sites on their surfaces for reversible and irreversible sorptions, and (iv) sorption affinity of radionuclides onto their available sorption sites (quantified by the sorption distribution coefficients). A multiple-layer sorption process is not considered in the TSPA–LA model. Organic colloids are considered unimportant at the Yucca Mountain site, because humic substances are not abundant in the Yucca Mountain environment.

A schematic representation of the irreversible and reversible association of radionuclides with mobile colloids and stationary corrosion products in the in-package environment and EBS is shown in Figure 2-1. Radionuclides associated with each colloid type and stationary corrosion product are listed in Table 2-1.

7

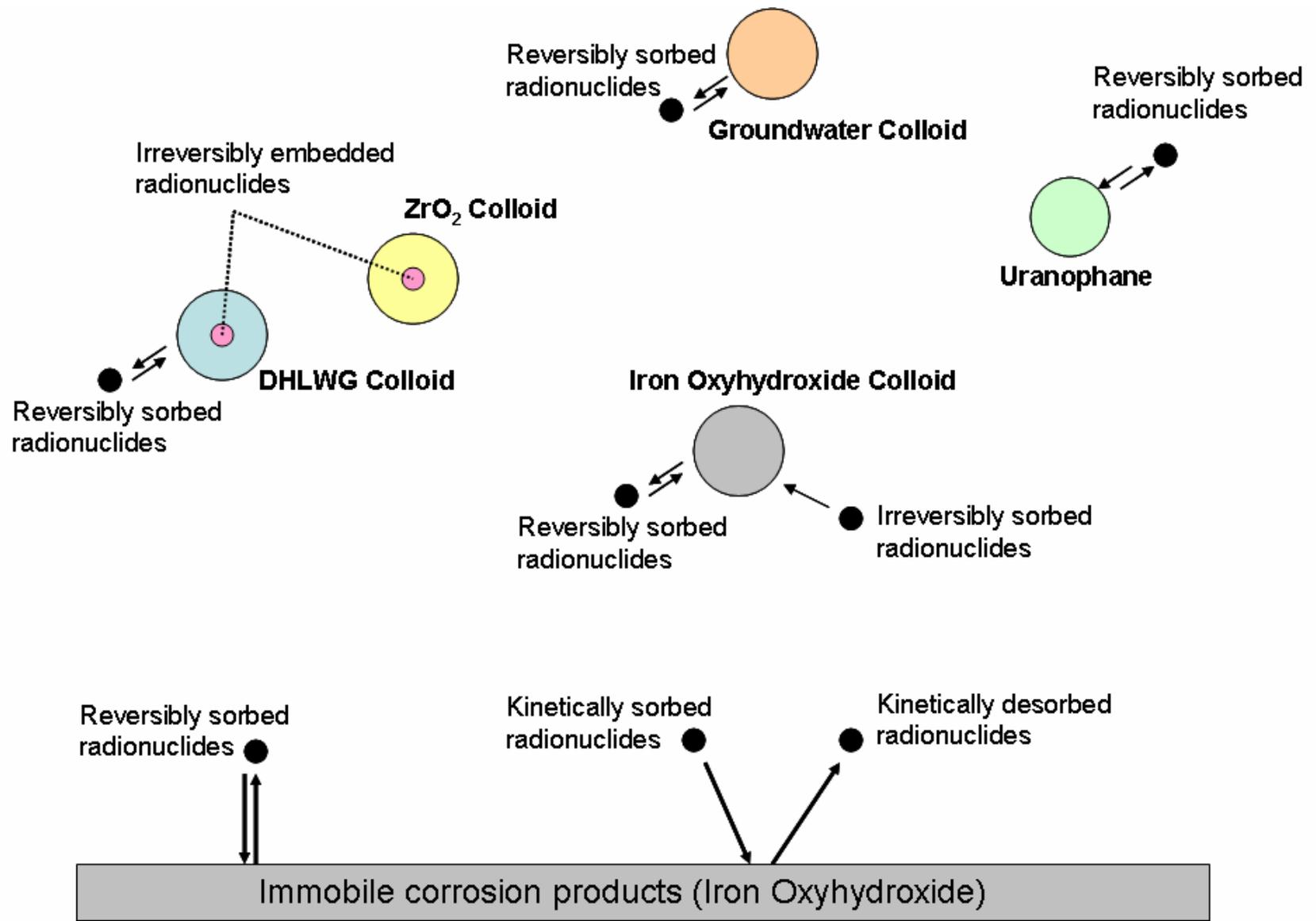


Figure 2-1. A Schematic Representation of Radionuclides Reversibly or Irreversibly Associated (or Sorbed Onto) Different Colloid Types and Stationary Corrosion Products. Radionuclides Associated With Colloid Types Are Listed in Table 2-1.

Table 2-1. Radionuclides Reversibly or Irreversibly Associated With (or Sorbed Onto) Different Colloid Types and Stationary Corrosion Products					
Domain		Irreversible Association	Reversible Sorption	Kinetic Sorption	Kinetic Desorption
Mobile Colloid	smectite (DHLWG)*	plutonium americium	plutonium americium thorium protactinium cesium		
	ZrO ₂	plutonium americium			
	uranophane		plutonium americium thorium protactinium cesium neptunium radium tin		
	iron oxyhydroxide		uranium thorium neptunium	plutonium americium	
	smectite (groundwater)		uranium neptunium tin radium		
Immobile Corrosion Products			uranium thorium neptunium	plutonium americium	plutonium americium

*Note: DHLWG–Defense High-Level Waste Glass

2.3 Stability of Colloids

Theoretical calculations and laboratory data were used to determine the stability of modeled colloidal suspensions (Sandia National Laboratory, 2007a). Ionic strength, pH, colloid–colloid interactions, and colloid concentrations of water entering the waste package from the surrounding drift are used in the stability calculations. The stability ratio, W , of 10 is used (as long as there are no significant changes in pH and ionic strength) above which colloidal suspension remains stable. DOE considered this stability ratio, based on the Derjaguin-Landau-Verwey-Overbeek theory, to be reasonable due to expected low ionic strength and dilute colloid concentrations at the potential repository site (Sandia National Laboratory, 2007a).

In the DOE abstraction, the stability ratio was defined in terms of the relative strength of the total potential energy, W_T (associated with the sum of the repulsive electrostatic forces and attractive van der Waals potentials), between two particles in comparison to the potential energy between two particles due to attractive van der Waals potentials only, W_{vdW} . Hence, the stability ratio is mathematically expressed as $W = W_T / W_{vdW}$.

DOE considered the implementation of the Derjaguin-Landau-Verwey-Overbeek theory to be bounding (Sandia National Laboratory, 2007a), because it does not address physical filtration and thin-film straining of colloids (immobilization of colloid particles whose sizes are larger than film thickness on fracture walls). Neglecting these processes would lead to less removal of colloids from flow zones. The representative colloid size, effective surface potential, Hamaker constant (used to determine the interaction strength between two particles in the van der Waals potentials), and the interaction (surface) depth (the depth at which the electrostatic double layer extends from the surface into the bulk solution) on particle surfaces in the van der Waals potentials are the direct inputs to the TSPA–LA colloidal suspension stability calculations. The additional required inputs to the stability model are the ionic strength and pH of the in-package fluid resulting from reaction with the waste and the ionic strength and pH of the seepage water entering the drift.

In Derjaguin-Landau-Verwey-Overbeek theory, surface potential varies with the fluid ionic strength and pH. At a given pH, the surface potential can be computed as a function of fluid ionic strength. At the threshold $W = 10$, there must a single ionic strength value at a fixed pH; the corresponding ionic strength is the ionic strength threshold (IST).⁷

For stability calculations for the representative colloids in suspension, best-fit curves for the surface potential and pH at different fluid ionic strengths were constructed (SP-pH curve) by using experimental data (Sandia National Laboratory, 2007a). Then, for $W = 10$, a surface potential is computed from the Derjaguin-Landau-Verwey-Overbeek theory. Subsequently, for a given pH and surface potential, the corresponding ionic strength is read from the SP-pH curve. Hence, the calculated ionic strength is the IST corresponding to $W = 10$. The recursive execution of this calculation for different pH values is used to construct the IST versus pH curve (IST-pH curve). The best fit to the IST-pH curve provides an empirical relation between the IST and pH to be used in the TSPA–LA model.

In the implementation phase, the ionic strength of the in-package fluid (or in-drift seepage fluid represented by properties of invert fluid) is compared with the IST value on the IST-pH curve corresponding to in-package (or in-drift) pH. If the in-drift (or in-package) fluid ionic strength exceeds the IST, then the corresponding colloidal suspensions are unstable. Otherwise, they are stable for that particular geochemical condition. The stability condition determines the mass concentration of colloidal suspensions at that timestep, as discussed in Section 2.7.

In summary, DOE uses the empirical IST-pH curve to determine whether the colloidal suspensions are stable in the in-package environment and EBS. If the colloidal suspensions are stable, the empirical colloid mass distribution functions are sampled to calculate the colloid mass concentrations; otherwise, the colloid mass concentrations are set to their minimum values. Additional DOE observations on the stability of colloidal suspensions follow (Sandia National Laboratory, 2007a):

- Smectite clay colloids (derived from DHLWG)—The pH versus ionic strength stability diagram is constructed for pH in the range of 1.5–9. DOE assumed that for $\text{pH} < 1-1.5$, there would not be any clay particles. Moreover, the IST would likely not change for $\text{pH} > 9$. Smectite colloids are predicted to be very stable under in-package chemistry conditions.

⁷Ionic strength threshold is referenced frequently throughout this report; consequently, the acronym IST will be used.

- Iron oxyhydroxide colloids—Depending on colloid and water composition, iron oxyhydroxide colloids tend to be unstable for pH values in the range of 5–8.5. The stability of the iron oxyhydroxide colloids outside this pH range is determined by fluid ionic strength. For corrosion-generated colloids, hydrous ferric oxide or goethite is used for sorption calculations. Hematite is used as a modeled colloid for stability calculations.
- Zirconium oxide colloids—Between pH 7 and 9.3, ZrO_2 colloids are unstable irrespective of the ionic strength.
- Uranophane colloids—These colloids are expected to be stable under a wide range of pHs similar to the case of smectite colloids.

DOE used different stability criteria in the waste package and in-drift environments. Therefore, the concentration of radionuclides reversibly sorbed onto colloids exiting the waste package is recalculated based on the stability criteria reflecting the chemical condition in the drift (invert). DOE noted that the change in the chemical condition may affect the stable mass concentration of colloids and hence the sorbed mass concentration of radionuclides reversibly sorbed onto colloids.

2.4 Mass Concentration of Colloids

The mass concentrations of DHLWG (smectite) and ZrO_2 are obtained from plutonium–colloid mass concentrations. The stability criteria developed for these colloids are used to determine the mass concentration of plutonium colloids. For the rest of the colloid types, the range and discretized empirical distribution functions (fitted to experimental data) are used to determine the available colloid-mass concentrations in each timestep in the TSPA–LA model (Sandia National Laboratory, 2007a). If the colloidal suspensions are stable, then the colloid-mass concentration at a particular timestep is sampled from the discretized empirical distributions to account for uncertainties. If the colloidal suspensions are unstable, the mass concentration of colloids is set to either a lower bound of the empirical distribution or to a prespecified minimum colloid concentration value.

2.4.1 Smectite (DHLWG) Colloids

In the abstraction, the mass concentration of DHLWG colloids is determined from irreversibly embedded plutonium–colloid mass concentrations in a stepwise process. The empirical uniform distribution was constructed for the plutonium–colloid mass concentration based on findings from the degradation of glass experiments. The colloidal plutonium concentration and particle concentrations (including all colloid types) were measured from high-surface area to volume-glass corrosion experiments (CRWMS M&O, 2001), and an empirical triangular distribution was proposed to relate the colloidal plutonium concentration to the colloid particle mass concentration. The lower bound, mode, and upper bound of the triangular distribution were set to 5×10^{-9} mol/L, 2×10^{-8} mol/L, and 2.5×10^{-8} mol/L.

In the first step of the abstraction, the stability condition is checked. In the second step, if the DHLWG colloids are stable, plutonium–colloid mass concentration is sampled from a uniform distribution in the range of 1×10^{-11} to 1×10^{-8} mol/L. Otherwise, colloidal plutonium concentration is set to the lower bound of the uniform distribution. Then the colloid mass concentration is computed by dividing the colloidal plutonium concentrations, sampled from the uniform distribution, by the scaling factor (the ratio of the colloidal plutonium concentration to the colloid particle concentration) sampled from the empirical triangular distribution.

2.4.2 Iron Oxyhydroxide Colloids

The range and the empirical distribution for the iron oxyhydroxide colloids derived from degradation of carbon steel rely on findings from flow experiments with carbon-steel miniature waste packages (Zarrabi, et al., 2003). The minimum and maximum iron oxyhydroxide colloid concentrations were 6.3×10^{-9} mol/L and 1.9×10^{-4} mol/L (for hematite). An empirical distribution was fitted to the experimental data between these minimum and maximum concentration limits. If the colloids are stable (based on the fluid ionic strength and pH), then the mass concentration of iron oxyhydroxide colloids is sampled from an empirical distribution as previously discussed; otherwise, it is set to 6.3×10^{-12} mol/L.

DOE noted that there were not sufficient data from stainless steel tests to reliably analyze colloid-mass concentrations. However, DOE constructed a distribution function for iron oxyhydroxide colloids derived from stainless steel based on its assessment of expected corrosion (Sandia National Laboratory, 2007a). DOE acknowledged that as stainless steel is less susceptible to corrosion than carbon steel, the overall colloid mass distribution would be expected to be less than carbon steel.

2.4.3 Zirconium Oxide Colloids

The range and the empirical distribution constructed for the ZrO_2 colloids rely on experimental data from immersion tests (Wilson, 1990). Similar to smectite (DHLWG) colloids, ZrO_2 colloid mass concentration is related to the colloidal plutonium mass concentration. In the abstraction, colloidal plutonium mass concentration is sampled from an empirical distribution (fitted to experimental data) in the range of 1×10^{-10} to 5×10^{-6} mol/L plutonium. If the colloids are unstable, the minimum value is set to 1×10^{-13} mol/L. The mass concentration of ZrO_2 colloids is computed by scaling the colloidal plutonium mass concentration sampled from the experimental data by a sampled cumulative distribution.

2.4.4 Uranophane Colloids

Because the uranophane colloids exhibited a stability profile similar to smectite clays, DOE assumed a similar population distribution is assumed for these two colloid types. The colloid mass range was obtained from unsaturated drip tests. Uranophane–colloid concentration varied from 1.7×10^{-9} to 3.4×10^{-4} mol/L. The minimum uranophane–colloid concentration was set to 1.7×10^{-12} mol/L for modeling purposes. Uranophane colloidal mass is determined by sampling the distribution when colloids are stable; otherwise, the minimum value of 1.7×10^{-12} mol/L is assumed when this colloid type is unstable.

2.4.5 Smectite (Groundwater) Colloids

The range and the empirical distribution DOE constructed for the groundwater colloids rely on combined experimental data from the Yucca Mountain site and Idaho National Laboratory. An empirical cumulative distribution is fitted to the colloid concentration data to capture the uncertainty in groundwater colloid concentrations for the TSPA–LA model analyses. The lower and upper bounds for the colloid concentration are set to 1.8×10^{-9} mol/L and 3.6×10^{-4} mol/L. If the colloids are unstable, the colloid concentration is set to 1.8×10^{-12} mol/L; otherwise, it is sampled from the empirical distribution for the groundwater colloid concentration.

2.5 Sorption/Desorption of Radionuclides Onto Colloids

Both irreversible and reversible attachment of radionuclides onto mobile colloidal particles and immobile collector surfaces are considered in the TSPA–LA model abstraction.

2.5.1 Irreversible Sorption

Three types of irreversible association of radionuclides with colloidal particles are considered in the abstraction.

- Irreversibly embedded/associated plutonium and americium in/with DHLWG wasteform colloids (smectite)
- Irreversibly embedded plutonium and americium in SNF-derived colloids (ZrO_2)
- Irreversible attachment of plutonium and americium onto iron oxyhydroxide colloids

Irreversible association of mass concentrations of plutonium and americium with DHLWG colloids and ZrO_2 colloids is described in Sections 2.7.1 and 2.7.3. In the TSPA–LA model, once the mass concentration of irreversibly associated plutonium is calculated, irreversibly sorbed americium is computed based on the mass concentration ratio of americium to plutonium in the inventory (Sandia National Laboratory, 2007a).

Irreversible attachment of plutonium and americium onto iron oxyhydroxide colloids is computed in the TSPA–LA model as a function of the specific surface area and mass concentration of iron oxyhydroxide colloids, dissolved concentrations of plutonium and americium, sampled target flux-out ratio, and other parameters (e.g., internally computed flow and diffusion rates).

The target flux-out ratio is the ratio of the total mass of radionuclides exiting the system that is reversibly or irreversibly associated with mobile colloids to the total mass of radionuclides exiting the system both in the dissolved phase and associated with colloids. The flux-out ratio is sampled from a uniform distribution in the range of 90–99 percent. The flux-out ratio of 95 percent is based on field observations at the Benham site (Kersting, et al., 1999) in which 95 percent of radionuclides that can potentially sorb onto colloids are transported by colloidal particles. The range of 90–99 percent is defined to account for uncertainties. Hence, the abstraction assumes that the large fraction of radionuclides leaving the system will be carried by colloids and only a small fraction of radionuclides will leave the system in the dissolved phase. This ratio (along with the aforementioned parameters) is subsequently used to determine the forward rate constant (for kinetically reversible sorption process) for irreversible attachment of plutonium and americium onto iron oxyhydroxide colloids. Hence, once the sorption distribution coefficients determine the mass concentration of reversibly sorbed radionuclides (by multiplying the aqueous phase concentration of radionuclides by their equilibrium sorption distribution coefficient), the forward rate coefficients obtained from the target flux-out ratio determine the radionuclides that are irreversibly sorbed onto mobile colloids.

Based on experimental data, the specific-area-based forward rate constant for plutonium irreversibly sorbed onto iron-oxide colloids is sampled in the TSPA–LA model from a log-uniform distribution in the range of $0.002\text{--}0.05\text{ m}^3\text{m}^{-2}\text{ yr}^{-1}$ [$0.079\text{--}1.97\text{ in}^3\text{in}^{-2}\text{ yr}^{-1}$]. According to Sandia National Laboratory (2007a, Table 6-24, p. 6-116), the same distribution is also assumed for americium irreversibly associated with iron-oxide colloids.

2.5.2 Reversible Sorption

The DOE abstraction simulates the reversible attachments of radionuclides onto corrosion product colloids and groundwater colloids (Sandia National Laboratory, 2007a). A list of radionuclides that DOE assumes to reversibly sorb onto particular mobile colloids and stationary corrosion products follows.

- Reversible attachment of plutonium, americium, neptunium, thorium, protactinium, radium, cesium, and tin onto uranophane colloids derived from SNF
- Reversible attachment of plutonium, americium, thorium, protactinium, and cesium to smectite colloids formed by degradation of DHLWG
- Reversible sorption of uranium, neptunium, radium, and tin onto groundwater (smectite) colloids
- Reversible attachment of thorium, neptunium, and uranium on iron oxyhydroxide colloids and stationary corrosion products

In the DOE abstraction, highly sorbing radionuclides are, in general, plutonium, americium, protactinium, radium, thorium, cesium, and tin. The medium sorbing elements are neptunium, selenium, strontium, and uranium, and they are evaluated for their importance for colloid-facilitated transport. Uranium was chosen because it is the dominant element within the waste, and its daughters are important for long-term performance. Neptunium was chosen because it is a major dose contributor in the earlier versions of the TSPA model. Strontium was not chosen due to its very short half life. Selenium was not chosen, because it exhibits low sorption in the absence of organics. Hence, the complete list of elements DOE considered in the EBS colloid-facilitated transport abstraction includes plutonium, americium, protactinium, radium, thorium, cesium, tin, uranium, and neptunium (Sandia National Laboratory, 2007a).

2.5.3 Reversible Competitive Sorption (Sorption Capacity Model)

In the TSPA–LA model, a simplified sorption capacity model based on time-variant radionuclide concentrations and their sampled K_d values was implemented to model competitive reversible sorption of radionuclides onto available mobile sorption sites (on colloid surfaces). The available sorption sites are linearly partitioned among the radionuclides based on their maximum allowable K_d (computed by using the radionuclide mass concentrations from the previous timestep) and their sampled K_d values (the maximum K_d varies with the temporal changes in radionuclide concentrations). At a given timestep, the K_d value is set to the minimum of the sampled K_d and the maximum allowable K_d . In calculating K_d , the maximum number of available sites for reversible sorption is described as a function of the available reversible sorption sites. The pH dependence of the sorption process is not addressed in the model.

A Langmuir isotherm relationship is used to calculate the percentage of coverage on the colloid surface as a function of the dissolved radionuclide concentration and an adsorption constant. The reversible sorption capacity of colloids is computed by the product of experimentally determined (and/or recommended) total available surface area and the density of the reversible sorptive sites on colloid surfaces. The surface area and site density of smectite colloids are set to 10–100 m^2/g and 2 sites/ nm^2 . Similarly, the surface area and site density of uranophane colloids are set to 30 m^2/g and 2 sites/ nm^2 .

In the DOE abstraction, the reversibly sorbed radionuclide mass associated with mobile colloids is computed by the product of the dissolved radionuclide concentration, the sorption distribution coefficient for that radionuclide, and the colloid mass concentration.

2.5.4 Sorption Distribution Coefficients K_d and K_c

In the TSPA–LA model, equilibrium sorption distribution coefficients are used to partition radionuclides between solid (stationary and mobile) and dissolved phases. Because the specific surface area of a colloidal phase could be larger than that of its common mineral phase, the sorption distribution coefficients, K_d , were adjusted accordingly in the TSPA–LA model (Sandia National Laboratory, 2007a).

The ratio of radionuclide mass concentration reversibly sorbed onto colloids to the dissolved radionuclide mass concentration is K_c . This parameter is equivalent to the product of the distribution coefficient, K_d , of the radionuclide and the colloid-particle concentration (K_d is defined as a function bulk density of the solid phase, whereas K_c is defined in terms of concentration of colloids). Hence, DOE uses K_c to estimate the significance of the colloid-facilitated transport of a particular radionuclide in a particular time period, given that mass concentration of a particular colloid type may change based on changes in chemical conditions.

Uranophane Colloids

The range of K_d for plutonium, americium, neptunium, thorium, protactinium, radium, cesium, and tin onto uranophane colloids was obtained from literature data (Sandia National Laboratory, 2007a). Within the upper and lower bounds, all K_d s are assumed to be log-uniformly distributed. The highest K_d s are those for plutonium, americium, thorium, and protactinium. DOE noted that no experimental data were available to independently confirm these parameter values. Because of the relatively low K_d values for sorption of radionuclides onto uranophane colloids, DOE considered uranophane colloids to be relatively unimportant as a transport mechanism.

Iron-Oxide (Corrosion Product) Colloids

The range of K_d for neptunium, thorium, and uranium onto iron-oxide and smectite colloids was determined based on experimental data from various literature sources. All K_d s are assumed to be log-uniformly distributed. As discussed in Section 2.5.2, reversible attachment of only thorium, neptunium, and uranium on iron oxyhydroxide colloids is considered in the TSPA–LA model.

The sorption of radionuclides onto hydrous ferric oxide and goethite is handled by a competitive sorption model that evaluates the competition between actinides (uranium, neptunium, plutonium, americium, and thorium) and nickel for a limited number of sites. DOE noted that although nickel is not transported in the TSPA–LA model abstraction, it is a major potential sorbing ion from the steel alloys and its competition for sorption sites is considered in estimating the sorption of radionuclides. The competitive sorption model contains both reversible sorption for uranium, neptunium, and thorium onto hydrous ferric oxide and goethite, as well as kinetic sorption–desorption for plutonium and americium, where slow desorption kinetics are applied to the stationary corrosion products.

2.6 Sorption/Desorption of Radionuclides Onto Immobile Corrosion Products

Colloid capture on solid surfaces is not described in the TSPA–LA model. Equilibrium sorption of uranium, thorium, and neptunium onto stationary corrosion products (iron oxyhydroxide) is included. Kinetic reversible sorption of plutonium and americium onto (with slow desorption from) stationary corrosion products (Figure 2-1) is formulated as a first-order reaction process and is a function of the specific surface area of the stationary corrosion products, the forward (or backward) reaction rate coefficient, and the aqueous (or sorbed) concentration of radionuclides. Kinetic sorption of plutonium and americium onto stationary corrosion products and mobile colloidal particles is simulated using the same forward rate constant. Unlike for colloidal particles, kinetic desorption of plutonium and americium from stationary corrosion products is considered in the TSPA–LA model (Table 2-1). Kinetic sorption and slow desorption of plutonium and americium is used for stationary corrosion products in the waste package for zero advective flux conditions or where colloids are unstable.

2.7 Radionuclide Mass Concentrations Associated With Irreversible Colloids

2.7.1 Smectite Colloids Associated With DHLWG

Only plutonium and americium are considered to be irreversibly sorbed onto DHLWG colloids (Sandia National Laboratory, 2007a,e). If DHLWG colloids are stable, then a colloidal plutonium concentration is sampled from a uniform distribution in the range of 1×10^{-11} to 1×10^{-8} mol/L (the cumulative distribution function is empirically generated from glass degradation experiments). Otherwise, irreversibly sorbed colloidal plutonium mass concentration is set to the lower bound of the uniform distribution. Concentration of irreversibly sorbed americium is computed based on the fraction of americium compared to plutonium in the inventory.

2.7.2 Iron Oxyhydroxide Colloids

Only plutonium and americium are considered to be irreversibly sorbed onto iron oxyhydroxide colloids. The mass of plutonium and americium irreversibly sorbed onto mobile iron oxyhydroxide colloids is computed using the irreversible, kinetically determined, competitive sorption model (Section 2.5.1). The irreversible attachment rate is limited by the available surface area of iron oxyhydroxide colloids.

2.7.3 Zirconium Oxide Colloids

Only plutonium and americium are considered to be irreversibly sorbed onto CSNF colloids (Sandia National Laboratory, 2007a,e). Plutonium–colloid mass concentration is obtained by sampling a fitted cumulative distribution function to experimental data for ZrO_2 obtained from immersion tests. If the ZrO_2 colloids are stable, plutonium colloid mass concentration is sampled from the experimental data; otherwise, it is set to the lower bound. Concentration of irreversibly sorbed americium is computed based on the fraction of americium compared to plutonium in the inventory.

2.8 Radionuclide Mass Concentrations Associated With Reversible Colloids

2.8.1 Smectite (DHLWG) Colloids

The mass concentration of plutonium, americium, thorium, protactinium, cesium, neptunium, uranium, tin, and radium reversibly sorbed on smectite colloids derived from DHLWG is given by the product of the mass concentration of DHLWG colloids, the concentration of radionuclides in the solution, and the surface-area-based distribution coefficient. The mass concentration of DHLWG colloids is obtained from sampled, irreversible plutonium–colloid mass concentrations (Section 2.4.1.).

2.8.2 Iron Oxyhydroxide Colloids

DOE uses a competitive sorption model (Section 2.5.3) to calculate the reversible sorption of thorium, neptunium, and uranium with iron-oxyhydroxide colloids. In the TSPA–LA model, mass concentrations of reversibly attached colloids are computed as the product of the mass concentration of mobile iron-oxyhydroxide colloids, the surface-area-based sorption distribution coefficient (mechanistically determined by the model), and the dissolved radionuclide concentration.

2.8.3 Uranophane Colloids

If the uranophane colloids are unstable, then the mass concentration of uranophane colloids is set to the minimum value (1×10^{-6} mg/L); otherwise, it is sampled from an empirical distribution. The mass concentration of plutonium, americium, neptunium, thorium, protactinium, radium, cesium, and tin reversibly sorbed on uranophane colloids derived from CSNF and DSNF is computed as the product of the mass concentration of uranophane colloids, the concentration of radionuclides in the solution, and the surface-area-based distribution coefficient of radionuclides.

2.8.4 Smectite (Groundwater) Colloids

The concentration of uranium, neptunium, radium, and tin reversibly attached on groundwater (smectite) colloids is computed by the product of the mass concentration of the groundwater colloids, the surface-area-based sorption distribution coefficient, and the dissolved concentration of radionuclides.

2.9 Alternative Models

Three alternative conceptual models were analyzed but not used in the DOE abstraction (Sandia National Laboratory, 2007a).

2.9.1 Two-Site Kinetic Model

The two-site kinetic model involves both fast and slow sorption rates. DOE excluded this alternative model because there were no long-term experimental data (beyond 150 days) to reliably estimate the slow sorption rate.

2.9.2 Rate of Colloid Generation Model

Radionuclide and colloid releases from DHLWG were considered to be a two-step process involving (i) alteration of the glass wasteform and precipitation of colloids and (ii) spallation of colloid-sized fragments from the alteration products. The rate of radionuclide production from DHLWG was expressed as a power function of altered glass mass and a scaling factor. Once the released mass of radionuclides is determined, the mass is distributed between clay layers on altered DHLWG surfaces, mobile colloids, immobile secondary phases, and the dissolved phase. DOE excluded this model because there is a significant uncertainty in extending laboratory findings on the occurrence of spallation (Sandia National Laboratory, 2007a,e).

2.9.3 Mechanisms of Colloid Generation

This alternative model considers the flow-rate dependence of the entrainment and mobilization of wasteform colloids. DOE excluded it because of insufficient support in the scientific literature to indicate mobile colloid generation at the unsaturated flow rates anticipated in the repository waste-package environment.

2.10 Uncertainties

DOE noted that uncertainties in the TSPA–LA model parameters result largely from temporal and spatial scaling and extrapolation of the physical and chemical conditions of data acquisition (Sandia National Laboratory, 2007a,e). Sources of uncertainty involve (i) extrapolating experimental data obtained over a short time period (days to years) to the compliance period; (ii) assuming a continuous supply of colloids; (iii) having difficulty extrapolating and upscaling experimental conditions [e.g., wasteform surface area, flow rate and flow mode (batch versus flow through), heterogeneities in colloid sizes and shapes] to the repository scale analyses; and (iv) experiencing uncertainties in the stability ratio, Hamaker constant, surface potential of colloids in the EBS, and the presence of oxidizing versus nonoxidizing conditions.

As for the uncertainties associated with the sorption processes, DOE noted that the limited accuracy of the linear sorption isotherm in predicting solute concentrations sorbed onto solids and in the dissolved phase is an important factor. Moreover, DOE noted that the TSPA–LA model does not include high redox potentials and explicit pH dependency of K_d . For strongly sorbing radionuclides, such as plutonium and americium, the performance assessment model is uncertain, because site-specific sorption isotherms that describe the relative concentrations of aqueous and sorbed phase radionuclides were not available (Sandia National Laboratory, 2007a,e).

In the TSPA–LA model abstraction, uncertainties are addressed by providing ranges, probability distributions, and bounding assumptions as appropriate for each given parameter or process.

3 SUMMARY

Colloid-associated radionuclides could migrate faster than the dissolved phase radionuclides because the stable colloidal suspensions could migrate faster than the average flow velocity and carry higher concentrations of radionuclides especially in high velocity zones (colloids avoid low velocity zones due to the size exclusion effects). The relatively lower residence time of radionuclides sorbed onto colloids in flow zones could result in higher radionuclide release rates from the potential repository. Also, kinetically strongly sorbing radionuclides (e.g., plutonium and americium) could move by attaching themselves onto (or being embedded into) mobile

colloids; otherwise, they could strongly sorb onto stationary surfaces delaying their releases from the potential repository and subsequent transport.

Current understanding of the DOE abstraction for colloid-facilitated radionuclide transport in the waste-package environment and the EBS is schematically displayed in Figure 2-1. Radionuclides associated with particular colloid types and stationary corrosion products are listed in Table 2-1. The importance of colloid-facilitated radionuclide transport in the waste-package environment and EBS is largely determined by the mass concentration and stability of different types of colloidal suspensions, their capacity for radionuclide uptake, and the mass concentration of radionuclides. Plutonium and americium irreversibly sorbed onto iron oxyhydroxide colloids and irreversibly associated with ZrO_2 and DHLWG colloids would likely be important because the irreversible colloids are not subject to trapping at the air–water interface and filtering in the waste packages and EBS. Moreover, because smectite colloids (DHLWG and groundwater colloids) are expected to be stable in the Yucca Mountain environment, the reversible attachment of radionuclides onto smectite colloids could also be important.

DOE has noted that colloid-facilitated radionuclide transport is the least important for uranophane colloids in the in-package and in-drift environment for all radionuclides considered in the abstraction (Sandia National Laboratory, 2007a). This is based on the relatively low K_d values for radionuclides that reversibly sorb onto uranophane colloids. Hence, if other colloid types are present in the system in sufficient mass concentrations and remain stable, radionuclides will preferentially sorb onto other colloid types instead.

4 REFERENCES

CRWMS M&O. “Colloid-Associated Radionuclide Concentration Limits.” ANL–EBS–MD–000020. Rev. 00 ICN 01. ACC: MOL.20010216.0003. Las Vegas, Nevada: CRWMS M&O. 2001.

Kersting, A.B., D.W. Eford, D.L. Finnegan, D.J. Rokop, D.K. Smith, and J.L. Thompson. “Migration of Plutonium in Groundwater at the Nevada Test Site.” *Nature*. Vol. 397, No. 6714. pp. 56–59. 1999.

Sandia National Laboratories. “Waste Form and In-Drift Colloids-Associated Radionuclide Concentrations: Abstraction and Summary.” MDL–EBS–PA–000004. Rev. 03. Las Vegas, Nevada: Sandia National Laboratories. 2007a.

_____. “In-Package Chemistry Abstraction.” ANL–EBS–MD–000037. Rev. 04. Las Vegas, Nevada: Sandia National Laboratories. 2007b.

_____. “Engineered Barrier System: Physical and Chemical Environment.” ANL–EBS–MD–000033. Rev. 06. Las Vegas, Nevada: Sandia National Laboratories. 2007c.

_____. “Dissolved Concentration Limits of Elements with Radioactive Isotopes.” ANL–WIS–MD–000010. Rev. 06. Las Vegas, Nevada: Sandia National Laboratories. 2007d.

_____. “EBS Radionuclide Transport Abstraction.” ANL–WIS–PA–000001. Rev. 03. Las Vegas, Nevada: Sandia National Laboratories. 2007e.

Wilson, C.N. "Results From NNWSI Series 3 Spent Fuel Dissolution Tests." PNNL-7170.
ACC: NNA.199200329.0142. Richland, Washington: Pacific Northwest National Laboratory.
1990.

Zarrabi, K., S. McMillon, S. Elkonz, and J. Cizdziel. "Corrosion and Mass Transport Processes
in Carbon Steel Miniature Waste Packages." TR-03-003. Rev. 0. Task 34.
ACC: MOL: 20040202.0079. Las Vegas, Nevada: University of Nevada, Las Vegas. 2003.