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Alternative Conceptual Model for Colloid Generation from Commercial Spent Nuclear Fuel

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Summary

Yucca Mountain is the Department of Energy's potential geologic repository designed to store and dispose of commercial spent nuclear fuel (CSNF) and other high-level radioactive waste forms. If approved, the site would be the Nation's first geologic repository for disposal of this type of radioactive waste. Yucca Mountain is located in a remote desert on federally protected land within the secure boundaries of the Nevada Test Site in Nye County, Nevada. It is approximately 100 miles northwest of Las Vegas, Nevada. CSNF makes up most of the spent nuclear fuel that requires disposal at Yucca Mountain.

The waste-form degradation process models provide technically defensible methods for predicting the long-term capability of the waste forms to control radionuclide release from the immediate vicinity of the waste. These models were provided as eight key feeds to the Total Systems Performance Assessment: radionuclide inventory, in-package chemistry model, cladding degradation model, commercial spent fuel degradation model, high-level waste glass degradation model, other waste-form degradation models, solubility model, and colloid model. Colloid generation from CSNF has been deemed to require further qualification by the present waste-form colloid model. The present colloid model considers the effects of pH and ionic strength on the stability of ideal colloid phases. The location of the boundaries between pH and ionic strength regimes in which colloids are stable or unstable are defined together with the colloid mass concentration in each regime.

Colloids may have the potential to transport strongly sorbing radionuclide contaminants in soils and groundwater aquifers (McCarthy and Zachara 1989). Recent studies from the Nevada Test Site (NTS), a site with a similar geology to Yucca Mountain, have indicated the enhanced mobility of plutonium in the saturated zone, albeit in minute quantities, in association with various silicate minerals (Kersting et al. 1999). However, calculated flow rates for the NTS saturated zone are 1000 to 10,000 times higher than those calculated using ^{36}Cl migration analysis for the proposed Yucca Mountain Repository waste-package environment under unsaturated conditions (Tompson et al. 2000; CRWMS M&O 1999). Significant colloidal transport of thorium and rare-earth elements (REE), considered to be chemical analogs for plutonium, are postulated to be rare in unsaturated environments (Wood et al. 1997). The current Yucca Mountain models for colloids would have predicted extensive thorium and REE migration, given these phases' association with clay minerals and the colloidal stability of the minerals in both unsaturated and saturated environments.

Several studies have pointed to the effect of pore velocity on colloid and particulate migration. An extension of the Ryan and Gschwend (1994) empirical relationship for colloid release indicates that colloid production rates within the waste package should be negligible owing to the predicted low hydraulic conductivities. However, the most important aspect with respect to the behavior of colloids in an unsaturated environment is the presence of the air-water interface. Very little research has been attempted to understand the role of the air-water interface on limiting the generation of mobile colloids from a weathered waste-form surface. The colloid migration experiments and the conceptual and numerical models developed under various vadose-zone migration programs have direct applicability to colloid-generation processes in the waste package. Thin-film straining (filtration) could retard colloid migration in unsaturated environments (Wan and Tokunaga 1997). Mathematical models adopted by Lenhart and Saiers (2002) could be the basis for an alternative model for colloid generation to supplement those presently proposed in the Yucca Mountain Project colloid models.

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Glossary of Definitions and Acronyms

AMR   Analysis and Model Report

CRWMS   Civilian Radioactive Waste Management System

CSNF   Commercial Spent Nuclear Fuel

DHLWG   Defense High-Level-Waste Glass

DLVO   Deryagin and Landau, and Verwey and Overbeek

DOE   U.S. Department of Energy

IR   Infrared

M&O   Management and Operations

NTS   Nevada Test Site

PA   Performance Assessment

PZC   Point of Zero Charge

REE   Rare-Earth Elements

SEM   Scanning Electron Microscopy

TEM   Transmission Electron Microscopy

UOH   Uranyl Oxide Hydrate

XRD   X-Ray Diffraction

YMP   Yucca Mountain Project

Definitions

Colloid A finely divided dispersion of one material in a second continuous phase (i.e., water). Colloidal particles are generally between individual molecules and macroscopic objects. A convenient limit is that a colloid is <1 μm in at least one dimension.

Darcy's law The velocity of flow through a porous medium is directly proportional to the hydraulic gradient assuming that the flow is laminar and inertia can be neglected.

Diffusion The random thermal motion of molecules or colloidal particles that gives rise to intermixing and collisions. The mean square displacement x^2 rather than the displacement, x, increases linearly with time, t. The diffusion constant, D, is given by: $D = x^2 / t$.

DLVO Theory DLVO theory accounts for the interaction between charged colloidal particles. It is based on the sum of a van der Waals attractive potential and a screened electrostatic potential arising from the "double layer" potential screened by ions in solution. The name DLVO comes from the two groups who separately developed this model: Deryagin and Landau, and Verwey and Overbeek.

Double Layer Interactions Ionized particles in aqueous solution interact with each other by electrostatic forces. The simple charged interactions are moderated by two effects: first, counter-ions will tend to associate at least loosely with opposite charges; second, the bulk concentration of ions in solution screens those electrostatic forces. These forces can be calculated by solving the Poisson-Boltzmann equation to determine the distribution of charged species given a thermal distribution of energies.

Flocculation The process of particle-particle aggregation leading to colloid sedimentation.

Hydraulic Conductivity The extent to which a given substance allows water to flow through it, determined by such factors as sorting and grain size and shape.

Hydrophobic A molecule or a part of a molecule that repels contact with water or an aqueous phase.

Pendular Ring Discontinuity When the water content in a rock is low, as in unsaturated environments, the water is trapped in rings around the contact points of the rock or mineral grains, called pendular rings. Colloid immobilization will depend on the probability of pendular discontinuity and also on the ratio of the colloid size to the film thickness. Pendular discontinuity increases as the moisture content decreases. The particles are trapped at the air-water interface film

unless the film thickness increases because of increasing moisture content.

Van der Waal Forces

These forces arise from the interaction of fluctuating electric dipoles in materials. There is generally an attractive potential between molecules that varies as $1/r^6$ where r is the separation. The integration of these interactions over all parts of a particle can give rise to longer range attractions with an exponent much smaller than 6. These forces are commonly the dominant attractive interaction between colloidal particles or between particles and other large objects. When the separation is large, the dipoles will not fluctuate in phase, and the potential is reduced. This retarded potential between molecules will vary as $1/r^7$.

Zeta Potential

The zeta (ζ) potential of a colloidal particle is the interaction potential observed by hydrodynamic measurements such as electrophoresis. The force on an electric charge in an electric field is balanced by the viscous drag such that the particle moves at a constant velocity. The potential measured in this way can differ from those seen in static measurements or the titration of charge as it will depend on details of viscous drag (the hydrodynamic radius) and the screening of charge by ions in the solution. When the zeta potential is reduced to zero, repulsion among/between particles will be eliminated and flocculation will occur.

Mineral Names and Formula

Boehmite	$AlO(OH)$
Boltwoodite	$KH(UO_2)(SiO_4) \cdot 1.5\ H_2O$
Brockite	$(Ca,Th,Ce)PO_4 \cdot H_2O$
Goethite	$Fe^{3+}O(OH)$
Hematite	Fe_2O_3
Illite	$K(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2 \cdot H_2O]$
Meta-Schoepite	$(UO_2)_4O(OH)_6 \cdot 5H_2O$
Meta-Studtite	$UO_2(O_2)(H_2O)_2$
Rhabdophane-Ce	$CePO_4 \cdot H_2O$
Schoepite	$[(UO_2)_8O_2(OH)_{12}](H_2O)_{12}$
Studtite	$[(UO_2)(O_2)(H_2O)_2](H_2O)_2$
Smectite	$(Na,Ca)_{0.3}(Al,Fe)_{2-3}(Si,Al)_4O_{10}(OH)_2 \cdot nH_2O$
Uraninite	UO_2
Uranophane	$Ca(UO_2)_2(SiO_3OH)_2 \cdot 5H_2O$

Unit Abbreviations

°C	degrees Centigrade
g/cm^3	grams per cubic centimeter (density)
mm/yr	millimeters per year (water flow velocities—hydraulic conductivity)

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Contents

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1.0   Introduction

The U.S. Department of Energy (DOE) is planning to develop a site for long-term storage of radioactive waste products at Yucca Mountain in Nevada. Commercial Spent Nuclear Fuel (CSNF) represents the major source of radionuclides at Yucca Mountain; however, with respect to colloids, there remains uncertainty about the impact of CSNF on the total waste-form colloid source term or the total quantity of colloids generated from various waste forms in the repository. The predicted oxidation rate for CSNF is very high; present waste-form degradation models assume that CSNF will be completely converted to a suite of U(VI) secondary phases within 1000 to 2000 years after canister failure and contact with moisture (Budnitz et al. 1999). This suggests that models looking at colloid generation from CSNF should assume that the fuel has already been subjected to moist-air oxidation and been transformed into an aggregated mass of alteration products before flowing water is able to contact the fuel. Pacific Northwest National Laboratory is recommending an improved model for predicting colloid generation and transport from corroded CSNF.

The point of zero charge (PZC) for smectite clays (Tombacz et al. 1990) and uranyl oxide hydrates (UOH) (Parks 1965) is near pH 2 and pH 4, respectively. Because the groundwater pH at Yucca Mountain is dissimilar to the PZC, both colloidal smectite clays and UOH phases may be stable (van Olphen 1977). In natural environments, rare-earth elements (REE) and thorium are often found associated with phosphate phases intermixed with clays (Taunton et al. 2000), similar to that observed with corroded defense high-level-waste glass (DHLWG) (Bates et al. 1992; Feng et al. 1994; Buck and Bates 1999). However, colloidal transport of thorium and REE is virtually non-existent in unsaturated environments (Wood et al. 1997). This suggests that although REE- and thorium-bearing colloids may be generated, their transportation rate must be very low. The reason may be related to the heterogeneous structure of the smectite-clay-heavy-metal aggregates and how these structures originally formed from the parent rock. Most current performance assessment (PA) models for colloid migration rely heavily on knowledge of colloidal stability. For example, the present Yucca Mountain Project (YMP) Model for determining colloid concentrations within the waste package uses the stability of ideal smectite clay and iron oxy-hydroxides colloids (CRWMS M&O 2000). This is then used to determine the source-term for colloidal-assisted radionuclide migration. Could such stability-based models overestimate the importance of radio-colloid migration? For plutonium to be sorbed to iron-oxide colloids (i.e., goethite [$Fe^{3+}O(OH)$] and hematite [Fe_2O_3]), plutonium must first leach from the CSNF and be soluble in the liquid that contacts the iron oxide. It is likely that the sorption of plutonium to iron-oxide colloids will be minimal because of the very low solubility of plutonium, based on measurements from spent fuel (Finn et al. 1994), plutonium-bearing ceramics (Bakel et al. 1998; Morss et al. 2002), and DHLWG tests (Ebert 1995). Furthermore, design changes within the waste package could reduce the amount of iron oxides available.

Because the solubility of plutonium is so low, the main source of plutonium colloids may likely be primary colloids, those generated directly during the alteration of CSNF. The hypothesis of the alternative model proposed here is that spent-fuel corrosion in a humid environment generates sub-micron alteration phases that form in the corrosion rind, and these alteration forms contain plutonium. The release of these radionuclide-bearing colloids from the altered surface will be strongly dependent on the water-flow conditions as well as the alteration structure (phase distribution and mineral crystallinity). The model proposed here does not suggest that the electrical-surface characteristics are unimportant;

however, specific knowledge of the PZC of individual ideal particles may be poor predictors of colloid concentrations in the waste package because stability-based models do not account for the heterogeneity in colloid aggregates and changes in particle-particle interactions. Under limited environments, a flow-rate dependence on colloid release has been observed (see McDowell-Boyer 1992; Ryan and Gschwend 1994; Kretzschmar and Sticher 1998; Grolimund et al. 1998; Grolimund and Borkovec 1999), yet the precise reasons for these empirical relationships are still unclear. Shevenell and McCarthy (2002) have demonstrated the importance of a variable flow rate and the effect of periodic flow on colloid release. Changes in flow rate and ionic strength resulted in more particle mobilization than under steady-state conditions.

It is unknown whether the types of radionuclide-bearing phases that have been observed to form during waste-form corrosion tests will be prone to similar dependencies. In this alternative model, an empirical flow-rate dependence as described by Shevenell and McCarthy (2002) would be adopted, but additionally, the role of mineral diagenesis in a model waste-form system needs to be considered. This model will allow quantification of changes in particle release under different flow rates and different particle-particle interaction scenarios. Figure 1.1 presents a schematic diagram showing the possible processes that could result in colloid generation during waste-form corrosion. Alteration of a waste-form in an initially moist-air environment will result in an irregularly weathered surface. The properties of this altered surface will be very similar to any other porous media, such as vadose-zone soils. As water and air contact the weathered surface, aqueous colloids can be generated through condensation of released species in solution (e.g., smectite clay precipitation and actinide hydrolysis) and by sorption of released radionuclides onto pre-existing colloids. These processes are described in the present Yucca Mountain colloid model (CRWMS M&O 2000) and have been observed with corrosion tests on DHLWG (Bates et al. 1992; Feng et al. 1994; Buck and Bates 1999). The corroded waste form may produce colloids through changes in water chemistry and water influx rate, allowing particles to be released from the surface. Colloid release may be related to the water flow rate, which controls the thickness of a region of immobility on the surface of the waste-form. Furthermore, in unsaturated conditions where only a thin layer of water may be present, particles cannot be mobilized (termed thin-film straining or filtration). The partitioning of some particles to an air-water interface and/or bubbles, as shown in Figure 1.1, could retard transport under unsaturated conditions but may increase colloid concentrations in fully saturated conditions. The attachment to air-water interfaces depends on the hydrophobicity of the surfacial colloidal corrosion products. In DHLWG, this process is not expected to occur, as the dominant alteration product, smectite clay, is not hydrophobic. However, this retardation mechanism may occur with spent fuel.

The classical theory developed by Darjaguin, Landau, Verwey, and Overbeek (DLVO) (van Olphen, 1977) contends that colloid mobilization is activated by physical and/or chemical perturbations, which can change the forces between the colloid and fracture surfaces. Colloid mobilization requires that the changes in solution chemistry or changes in the hydrodynamic shear forces produce repulsive forces between the attached colloids and the fracture surface that exceed the attractive forces. However, large discrepancies exist between the predicted and observed detachment of particles under natural conditions, mainly because of the heterogeneous properties of the colloids and fracture surfaces (both in chemical composition and geometries), non-uniform flow velocity, and chemical heterogeneity of the infiltrating solution (e.g., Ryan and Gschwend 1994). Measurements of zeta potentials of heterogeneous weathered waste-form surfaces represent averages of these surfaces and will be poor predictors for colloid generation and stability (Elimelech et al. 2000). Likewise, the use of the zeta potentials of ideal phases,

such as smectite clays or iron oxides with pH, may not accurately reflect the heterogeneous nature of the altered waste forms and waste package. Therefore, predictions of particle stability as a function of ionic strength and pH may not provide the basis for a completely defensible colloid model for the Yucca Mountain repository as stability predictions do not provide information on the quantity of colloids generated.
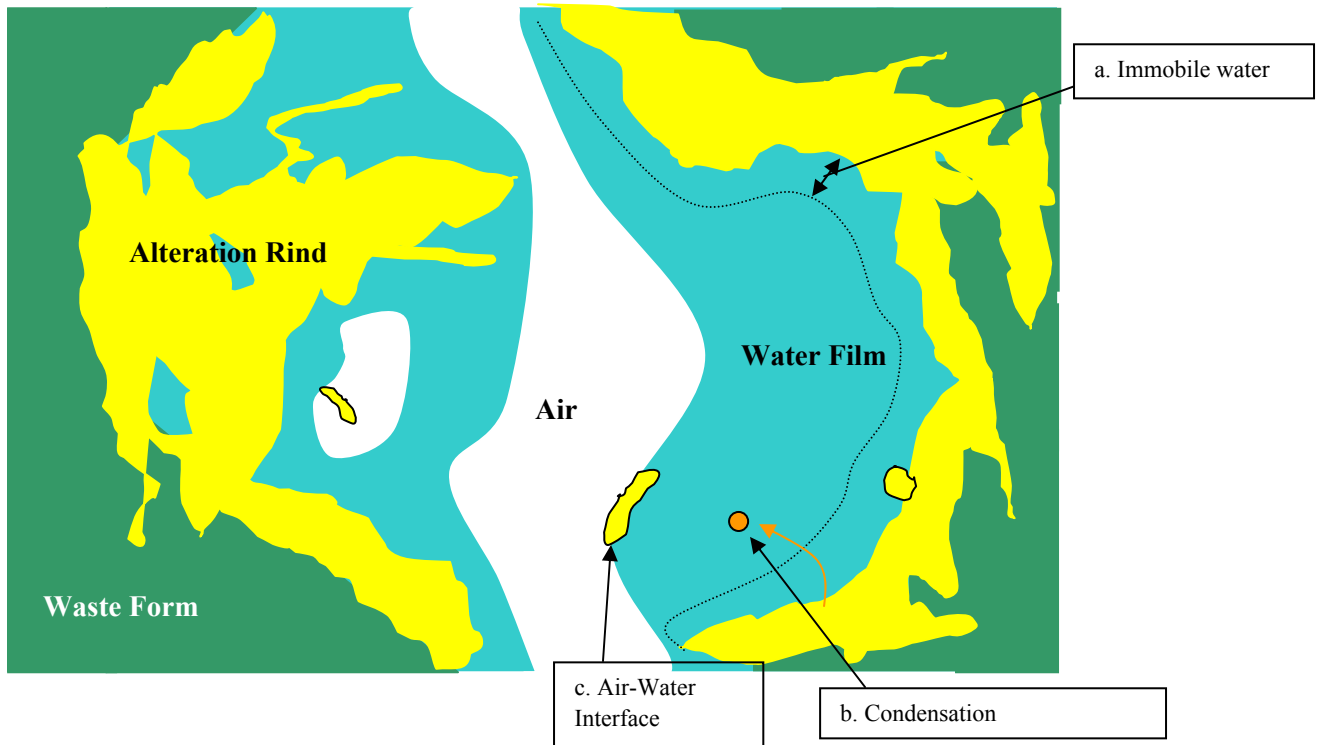
Figure 1.1.   Schematic Showing Three Mechanisms for Colloid Generation in the Waste Package. Waste-Form Moist-Air Corrosion Leads to the Development of an Irregular Surface Rind that is made up of Colloidal-Sized Alteration Phases. (a) Migration from the Immobile Contacting Film Depends on the Water Conditions (pH, ionic strength, flow rate); (b) Release of Species from the Corroding Waste-Form Leads to Precipitation (Condensation) of Colloids in Aqueous Solution, and (c) Partitioning of Hydrophobic Particles to the Air-Water Interface May Increase the Immobilization of Some Colloids.

2.0 Background

This section describes smectite clay colloids (especially as they relate to the Yucca Mountain Site) and various colloids formed from commercial spent nuclear fuel. Colloids formed from DHLWG consist predominantly of smectite clay substrate often containing discrete REE- or Pu-bearing phases entrained within the clay (Bates et al. 1992; Buck and Bates 1999). The waste-form colloid Analysis and Modeling Report (AMR) assumed that colloids derived from the waste form were all radionuclide-bearing smectite (CRWMS M&O 2000). The highly important finding of probable plutonium migration in groundwater at the Nevada Test Site (Kersting et al. 1999) has generated concern for the potential of radionuclide colloidal-assisted migration from the proposed Yucca Mountain repository. Yet the hydraulic conductivities determined for the Nevada Test Site (NTS) saturated zone (Tompson et al. 2000) are 1000-10,000 times higher than those anticipated for the unsaturated zone where the waste package is to be located.

The release of the CSNF colloidal aggregates from the surface of degraded/altered fuel will be a complex process due to several factors, including changes in water chemistry over time. One recent study on colloid release from altered fuel has highlighted the importance of cementing phases that bind various clays, quartz (SiO_2), and aluminum (boehmite) and iron oxides (goethite) in sediments (Liang et al. 2000). In the case of humid air alteration of CSNF, no binder phases are anticipated to be present. However, amorphous silicates and iron oxy-hydroxides (e.g., goethite) will be present in corroded DHLWG waste packages and could play a role in binding radionuclide-bearing colloidal aggregates together. At more distant points from the CSNF, the dissolution behavior of these binder phases could be key for mobilizing some particles. Corrosion tests generally contain poorly crystallized phases (Feng et al. 1994; Buck and Bates 1999) that formed under accelerated conditions. These may be more prone to mobilization than more slowly formed and more crystalline alteration rinds (e.g., natural REE and thorium-altered sediments). Natural clay deposits in unsaturated environments consisting of smectite and illite {ideally $K(Al,Mg,Fe)_2(Si,Al)_4O_{10}[(OH)_2 \cdot H_2O]$} silicate minerals and containing REEs have exceptionally low hydraulic conductivities (<0.8 mm/yr), and colloidal transport of REEs under these conditions is unknown (Johannesson and Hendry 2000). However, if the rate of CSNF alteration is rapid, submicron-sized secondary precipitates may form in the waste package.

2.1 Smectite Clay Colloids and Radiocolloids

Smectite clay [ideally $(Na,Ca)_{0.3}(Al,Fe)_{2-3}(Si,Al)_4O_{10}(OH)_2 \cdot nH_2O$] is a major colloidal alteration phase arising from the dissolution of DHLWG (Feng et al. 1994; Buck and Bates 1999). Smectites are also present in the Tuff rock at Yucca Mountain along with other silicate minerals (Bish and Vaniman 1985). As the PZC for smectite clays is near pH 2 (Tombacz et al. 1990), these colloids will probably be stable under most groundwater pH conditions (van Olphen 1977). However, flocculation may be accelerated in the presence of other particles, such as iron oxides, manganese oxides, and/or metal phosphates. Plutonium-, thorium-, and rare-earth-bearing phosphate colloids [structurally related to rhabdophane ($CePO_4 \cdot H_2O$) and brockite $(Ca,Th,Ce)PO_4 \cdot H_2O$] have been observed to be attached to smectite clay particles during laboratory corrosion tests on DHLWG (Bates et al. 1992; Buck and Bates 1999; Ménard et al. 1998). These particles are probably positively charged, as they were found associated with the negatively charged smectite clay particles. The colloidal behavior of smectite clays may be an important

parameter in determining the disposition of colloidal plutonium from corroded DHLWG under anticipated repository conditions.

In many of the corrosion tests conducted with nuclear waste forms, plutonium tends to follow REE, Th, and Am (Bakel et al. 1998; Buck and Bates 1999). This may justify using Th- and REE-bearing natural analogs to predict the possible migration of Pu from a geologic repository; however, plutonium chemistry is very complex and highly dependent on the environmental conditions. Hence, the use of Th and REE analog sites may be inaccurate at times. Studies by Wood et al. (1997) at the Cretaceous Idaho batholith is possibly the most intriguing natural analog site for colloids derived from waste forms. At this deposit, hydrothermal alteration of the Casto granite containing allanite $[(Ca,Mn,Ce,La,Y)_2(Fe^{2+}Fe^{3+},Al)_3O \cdot OH(Si_2O_7)(SiO_4)]$ to phosphate phases, such as monazite $[(La,Ce)PO_4]$ and rhabdophane $[(La,Ce)PO_4 \cdot 2H_2O]$, is almost directly analogous to the laboratory weathering experiments with borosilicate glasses. Many of these phosphate minerals are associated with silicates, including clays (Taunton et al. 2000; Wood et al. 1997). However, the occurrence of extensive colloid transport of REE and thorium under ambient conditions is rare. REE in Saskatchewan, Canada, have been found associated with carbonate complexes that strongly sorbed to the clay mineral fraction (Johannesson and Hendry 2000). At Oklo, Gabon, more than 90% of the fissiogenic REE and actinides are associated with the original uraninite matrix, and there was no evidence for colloidal migration from weathered regions (Hidaka and Holliger 1998).

Studies of anthropogenic sources of plutonium in the environment have had a mix of results that are difficult to explain. Colloidal particle migration was suspected as a contributor to plutonium contamination at Mortandad Canyon, New Mexico. The observed contamination was originally thought to demonstrate evidence for rapid plutonium and americium migration, but this theory has been shown to be incorrect (Marty et al. 1997). At Rocky Flats, Santschi et al. (2002) showed that colloidal plutonium was most associated with organic macromolecules and not with the more abundant iron oxides and clays. This behavior was suggestive of an electrostatic interaction between the plutonium colloids and organic surfactants within the soil. Dai et al. (2002) report that <4% of plutonium contamination was associated with colloids in soils at the Savannah River Site, South Carolina, owing to the higher oxidation state of the plutonium. Buck et al. (2004) found the plutonium became enriched relative to americium and REE at the surface of a spent fuel exposed to moist air over a period of years. These various studies illustrate that plutonium behavior is highly dependent on environmental conditions and source.

2.2 Colloids Formed from Commercial Spent Nuclear Fuel

Compared to the understanding of colloidal particle generation from DHLWG corrosion, comparatively less is known about CSNF. Only a limited number of test configurations and data have been examined. Finn et al. (1994) observed the formation of various colloidal uranium phases (e.g., schoepite-related structures) and REE-bearing phases in leachates from corrosion tests with spent fuels. However, at later times during the experiments, colloid release virtually stopped. However, presently, it is not possible to determine the reasons for the termination of colloid production. Yet, it is unlikely that the scenario of CSNF alteration in contact with an equilibrated J-13 (EJ-13) groundwater will occur. Wronkiewicz et al. (1996) also observed suspended particles of uranophane $[Ca(UO_2)_2(SiO_3OH)_2 \cdot 5H_2O]$ and uraninite (UO_2) within the leachates of tests on unirradiated UO_2, although the design of their experiment was significantly different from the Finn et al. (1994) CSNF tests and possibly allowed for greater particle

release. This report describes the ready formation of a stable colloidal suspension of meta-schoepite $[(UO_2)_8O_2(OH)_{12}](H_2O)_6$ from tests with unirradiated UO_2. The UOH phases were determined to be hydrophobic and became stabilized by attaching themselves to the air-water or non-polar-water interfaces, similar to observations in other colloidal systems (Wickman and Korley 1998). Depending on the solution conditions, the UOH particles were arranged in open diffusion-limited fractal aggregates or in tightly bound fractal structures that covered micro air bubbles. An increase in ionic strength tended to enhance the stability of the uranium-bearing micro-bubbles, probably by lowering repulsive forces and creating a more compact structure. These few examples suggest a significant potential for colloid generation from spent fuel if favorable conditions, such as saturation, exist.

2.3 Effect of Flow Rate

McDowell-Boyer (1992) addressed the mobilization of ideal spherical colloidal particles at the microscopic level. At this microscopic scale, there is competition between the London-van der Waals attractive forces and the electrical double layer (attractive/repulsive) forces between colloidal particles and the surface of the solid matrix. These forces lead to the idea of critical shear stress. McDowell-Boyer (1992) stressed the importance of flow-rate dependence on colloidal particle mobilization and concluded that the transport of colloids may be negligible unless the system has been subjected to physical or chemical alteration. By knowing the degree of these alterations and their influence on colloids, mobilization within the waste package could reduce the potential impact of colloid-facilitated transport of radionuclides on dose at Yucca Mountain. Bergendahl and Grasso (2000) determined that removal distributions were insensitive to aqueous chemistry (pH or ionic strength) and were dependent only on the flow rate. Below 2 mL/min, no colloid release was observed. As water infiltration rates are anticipated to be much lower than 2 mL/min over the lifetime of the repository, the adoption of a flow-rate dependence on colloid release may effectively screen out colloids from PA.

2.4 Air-Water Interface

The single most important aspect in an unsaturated environment is the presence of the air-water interface (Wan and Wilson 1994). Research from vadose-zone migration should have direct applicability to colloid-generation processes in the waste package. The concentrations of lead, iron, nickel, copper, and various organics have been found to be up to 50 times higher in the surface layer of a natural water body relative to the bulk water (Wan and Tokunaga 1998). This suggests that colloidal partitioning at air-water interfaces can be significant in natural systems. Many of the secondary phases that form during spent-fuel corrosion are very small (nanometers to micrometers), giving them high specific surface areas and high-surface-charge densities. As was shown earlier, these phases are, generally, hydrophobic and will partition strongly to the air-water interface (see Figure 1.1). These characteristics may make the uranyl phases efficient carriers of otherwise immobile, strongly sorbing metal ions. The mechanism of thin-film straining is a complex phenomenon caused by several mechanisms, including London van der Waals forces, Coulomb forces, hydrogen bonding, and hydrophobic forces. The actual nature of the hydrophobic mineral surface-air interaction continues to be a subject of intense interest and debate (Wickman and Korley 1998; Liu et al. 2003). Tests on other heavy-metal oxides reported here, including tungsten oxide (WO_3) and thorium oxide (ThO_2), demonstrated that these phases also exhibited attachment to air-water interfaces but not to the same degree as the UOH phases. Some limited data

available on plutonium oxide from the Plutonium Finishing Plant at Hanford indicate a similar behavior under some conditions.

3.0   Model Assumptions

The following assumptions are involved in the model presented in this report.

- Waste-form corrosion in a humid environment will result in the generation of immobile colloids on the weathered waste-form surface (Buck and Bates 1999; Bates et al. 1992; Finn et al. 1998; Buck et al. 2004). The rate of corrosion is taken from the respective corrosion rates for the waste forms (i.e., borosilicate glass and/or spent nuclear fuel).

- Spent-fuel corrosion is conservatively assumed to be relatively rapid in a humid environment [100 to 2000 years for complete conversion to U(VI) phases following breach of the canister and exposure to moisture (Budnitz et al. 1999)]. The fuel is altered to a series of uranyl-oxide-hydrate phases and plutonium-ruthenium-zirconium nano-precipitates (Finn et al. 1998; Buck et al. 2004).

- The amount of soluble plutonium released is assumed to be negligible. Hence, the attachment of plutonium to pre-existing colloids (e.g., iron oxy-hydroxides from corroded canisters and smectite groundwater colloids) is also considered negligible. The low solubility for plutonium is based on the results of static immersion tests with plutonium-bearing solids (Bates et al. 1992; Ebert 1995; Bakel et al. 1998; Buck and Bates 1999; Morss et al. 2002; Finn et al. 1998). All plutonium is considered to be retained within the alteration rind in nano-precipitates. Low pH (<3) conditions would increase the amount of soluble Pu.

- Particle attachment to the air-water interface is considered significant for hydrophobic-layered alteration phases, such as uranyl oxy-hydroxides. Air-water interfaces are the principal method for particle attachment in unsaturated environments (Wan and Wilson 1994; Wan and Tokunaga 1998).

- Smectite clays and UOH phases are stable with respect to groundwater conditions anticipated in the repository environment (Tombacz et al. 1990). Iron oxides derived from the corroded canister materials are assumed to play a role immobilizing dissolved plutonium and in the aggregation of other colloids in the waste package, but they have been ignored in this model.

4.0 Model Discussion

4.1 Empirical Observations and Models

Estimates of water flow at Yucca Mountain based on ^{36}Cl analysis are extremely low. The net infiltration estimates for the present-day are 4.6 mm/yr, and those from the more active glacial-transition climates were 15.6 mm/yr (CRWMS M&O 1999). This contrasts with hydraulic conductivities used by Kretzschmar and Sticher (1998) of 9×10^4 to 2×10^7 mm/yr for their experiments. The low flow rates at Yucca Mountain are impossible to replicate under laboratory conditions while still obtaining reasonable colloid-release data. However, hydraulic conductivities calculated from data obtained through the Nevada Test Site migration studies by Tompson et al. (2000) ranged from 7.3×10^4 mm/yr to 3.6×10^6 mm/yr. Tompson et al. (2000) claim some values were as high as 1.8×10^7 mm/yr; however, their values were taken from the saturated zone at Yucca Mountain. Ryan and Gschwend (1994) that the rate limiting step for colloid release was dominated by hydrodynamics and obtained a simple relationship between hydraulic conductivity (pore flow rate) (v) and particle detachment (k_{exp}). This may provided empirical rate equation for colloid release for pore flow ranges between 2×10^5 mm/yr and 2×10^7 mm/yr, which could be extend to the range described by Tompson et al. (2000). The Ryan and Gschwend (1994) derived a diffusion-limited release equation as:

$$k_{exp} = 10^{1.01\pm0.1} \, v^{0.84\pm0.02}$$

(4.1)

where v is the pore velocity in m/s and k_{exp} is a release rate per second. The pore velocity is defined by Darcy's Law, the flow rate divided by the cross sectional area of the experimental column times the porosity.

Assuming this equation can be extrapolated to the unsaturated zone Yucca Mountain hydraulic conductivities of 4.6 to 15.6 mm/yr (i.e., 1.45×10^{-10} m/s to 4.94×10^{-10} m/s), this would correspond to a colloid release rate of $\sim10^{-10}$/s.   As Darcy's Law is generally considered to be invalid for such very low hydraulic conductivities, direct use of this equation in this manner may be inappropriate. However, this relationship implies that colloidal migration from the waste-form surface should not occur in the waste-package environment. However, if the Tompson et al. (2000) values are applied to the Ryan and Gschwend (1994) equation, colloid migration could be extensive provided the possibility of colloid immobilization is excluded.

Ryan and Gschwend (1994) also showed that the activation energy for release was not accounted for in the simple DLVO theory. At present, this activation component is not known for particles of relevance derived from CSNF degradation. The release of colloidal particles should first depend on the magnitude of the inter-surface potential energy barrier (or sticking potential). At this point, release should be independent of flow because fluid motion is negligible at the particle surface (see Figure 1.1b). However, data from colloid-release experiments (Grolimund and Borkovec 1999) and also natural systems, such as from storm-water runoff (Shevenell and McCarthy 2002; Grout et al. 1999), suggest that changing water flow rates are an extremely important factor influencing colloid release. The longer the time for zero flow, the greater the initial particle release. It was theorized by Shevenell and McCarthy (2002) that diffusion within the immobile film was an important factor that should be considered. It is not apparent

whether time-dependent diffusion in the immobile film or changes in the thickness of the immobile film with flow are responsible for particle release.

Several models for predicting colloid release have been proposed that account for the dynamics of water flow. Govindaraju et al. (1995) developed a model for analyzing the detachment of particles from a soil column and their subsequent migration. The model assumed that flow rates are governed by Darcy's law, and changes in permeability were related to the porosity through the Kozeny-Carman equation. Porosity should be related to the attachment energies and the nature of the aggregating colloids. Lenhart and Saiers (2002) developed a mathematical model that incorporates a first-order rate law to simulate film straining and a second-order law to simulate partitioning to the air-water interface. Mass-transfer parameters of the model were sensitive to changes in the saturation level and the flow rate.

Knowledge of the energy barrier opposing release will be useful in determining particle-release characteristics. Models available for determining surface-charge potentials from zeta-potential measurements are nearly always inaccurate. This is because colloidal materials are inherently highly heterogeneous. However, this means that the data collected from ideal systems may not be easily incorporated into useful models. This proposed alternative model proposes adopting equations developed by Lenhart and Saiers (2002) to determine colloid concentrations derived from corroding spent fuel and waste glass.

4.2 Release Kinetics

Assessing the possibility of colloid release from a corroded surface requires a detailed understanding of the phenomena controlling particle deposition and release. This type of understanding and model development for colloid release in environmental science has typically required laboratory column experiments under well-controlled conditions, such as those performed by Ryan and Gschwend (1994) and Grolimund and Borkovec (1999). At present, data are unavailable for a spent nuclear fuel system; however, published models can be used to see their applicability to Yucca Mountain.

4.2.1 Advection Dispersion Model/Equations

Under steady-state saturated conditions, the transport of colloids through porous media can be described by the one-dimensional advective-dispersive transport equation (Kretzschmar and Sticher 1998; Grolimund et al. 1998; Grolimund and Borkovec 1999).

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} - kC \qquad (4.2)$$

where C = colloid concentration in solution
   t = elapsed time
   x = travel distance
   D = dispersion coefficient for colloid particles
   v = average travel velocity of the colloidal particles
   k = colloid deposition rate coefficient. If k = 0, there is no sorption on the colloid phase.

4.2.1.1 Activation Energy for Colloid Release

Grolimund and Borkovec (1999) have shown that the advection/dispersion methodology underestimates particle-concentration decay while predicting that cumulative mass rises faster than is observed experimentally. Their solution was to incorporate multiple populations of colloids with a distribution of release-rate coefficients using the following relationship:

$$k = k_0 \, e^{-E/RT} \tag{4.3}$$

where RT is the thermal energy, E is an activation energy, and k_0 is the fast-release-rate coefficient, which reflects the rate in the absence of an activation-energy barrier. If the distribution of rate coefficients depends on the distribution of activation energies, then k will have a thermal distribution.

4.2.1.2 Rate-Limited Transfer to Air-Water Interfaces

Lenhart and Saiers (2002) included rate-limited mass-transfer terms for particle retention within partially saturated sand columns. In their experiments, the deposition of silica colloids onto the thoroughly cleaned quartz sand was negligible, and colloid mass transfer was controlled solely by the presence of the air phase. Water flow in the unsaturated columns occurred simultaneously through films of water adsorbed to the sand grains, narrow water-filled pores, and connected pendular rings. The assumption of this model is that colloids that are either retained within thin-films or move to air-water interfaces are essentially immobilized. Lenhart and Saiers (2002) presented the one-dimensional form of the advection-dispersion equation (Equation 4.2) extended with source-sink terms to account for the attachment to air-water interfaces and fixation to thin-films. This new equation described the movement of colloids in their experimental columns.

The dispersion coefficient (D) from Equation 4.2 was made equal to qA_L/Θ and v, the velocity, to q/Θ where Θ is the moisture content, A_L is the longitudinal dispersivity, and q is the specific discharge rate.

The source and sink terms added to the advection-dispersion equation of Lenhart and Saiers (2002) can be more simply expressed as a colloid deposition rate coefficient (k) (as in Equation 4.2) as follows:

$$k = C(k_1 + k_2 \frac{X - S_{AW}}{X}) \tag{4.4}$$

where S_{AW} is the concentration of colloids associated with the air-water interface (mass of colloids per liter of air) and X is the retention capacity of the air-water interface (mass of colloids retained per liter of air).

Values of k_1 can be calculated from information on pendular ring discontinuity, film thickness, and flow rate:

$$k_1 = P(\Psi)\left(\frac{d}{w}\right)^{\beta} N v^{(1+h)} \tag{4.5}$$

where $P(\Psi)$ = probability of pendular ring discontinuity (expressed as a function of capillary
               pressure head, Ψ)
          d = colloid diameter
          w = film thickness
h, N, and β = empirical parameters that Wan and Tokunaga (1998) presumed constant for
               geometrically similar media.

Lenhart and Saiers (2002) used this modified second-order rate law to describe the deposition of inorganic colloids in saturated systems for conditions in which colloids and collectors possess opposite surface charges. According to Wan and Tokunaga (1998), colloid immobilization by film straining depends, in part, on the probability of pendular ring discontinuity and on the ratio of colloid size to film thickness. The probability of pendular ring discontinuity varies inversely with moisture content; in other words, the fraction of disconnected pendular rings increases from zero to unity as Θ decreases from its saturated value (i.e., $\Theta = n$) to its residual value (i.e., $\Theta = \Theta_r$, where Θ_r is the residual moisture content). As pendular rings disconnect, an increasing proportion of water flow and colloid transport is relegated to the adsorbed films of water that envelop the mineral grains. When the film width is greater than the colloid diameter, straining remains ineffective; however, when the film width is similar to or less than the colloid diameter, surface tension retains colloids against the mineral grain surfaces. Once trapped within thin films, particle escape does not occur unless the films expand owing to an increase in volumetric moisture content. A first-order rate law quantifies the temporal change in concentrations of colloids immobilized within thin films:

In addition to colloid retention within thin films of adsorbed water, colloids traveling within relatively large water channels and through connected pendular rings may diffuse to the air-water interface where they are captured by capillary forces. Wan and Wilson (1994) reported that the affinity of colloids for the air-water interface increases with particle hydrophobicity and that, once deposited, both hydrophobic and hydrophilic colloids are thermodynamically stable at the interface, irreversibly held by surface tension.

According to Lenhart and Saiers (2002), the modified advection-dispersion equation is appropriate for describing the one-dimensional transport of colloids through unsaturated media for cases in which colloid mass transfer is dominated by reactions within thin-water films and at immobile air-water interfaces. Lenhart and Saiers (2002) solved Equation 4.2 by using a finite-difference method with a predictor-corrector time-stepping scheme for zero initial concentrations, a first-type upper-boundary condition, and a zero gradient in concentration at the column base. They used the breakthrough data on silica transport to test this dual-rate-law model as well as to test the other models.

4.2.2 Kozeny-Carman Model

The model described by Govindaraju et al. (1995) assumes that flow rates are governed by Darcy's law, and the changes in permeability are related through the Kozeny-Carman equation. The first part of the model involves the removal of clay from a parent soil. This is analogous to removal of smectite clay weathering products from altered DHLWG or UOH and plutonium phases from altered CSNF. The primary agents contributing to colloid detachment were the shear stresses exerted by the local flow velocity. The second part involves transportation in the pore water (analogous to the weathered waste package), and the third part is the deposition of colloids.

The flow rate over the corroded waste form surface may be approximated by:

$$q(x,t) = \frac{k(x,t)}{\mu} \, A\rho g H \Big/ L \tag{4.6}$$

where μ = dynamic viscosity of water
   A = cross-sectional area of the corrosion rind
   ρ = density of water
   g = gravitational constant
   H = hydrostatic head of water acting on the sample
   L = length of the waste form
   $k(x,t)$ = absolute permeability of the porous medium.

The colloid removal term was expressed as:

$$R = \rho_s \sigma \left(\frac{T_c}{\rho_c - qC} \right) \tag{4.7}$$

where T_c = flow transport capacity
   σ = a measure of detachability
   ρ_s = mass density of colloids on the waste form
   ρ_c = density of colloids suspended.

Equation 4.7 relates particle removal to the difference in transport capacity of the flow and the actual colloidal suspension in the flow. Assuming that all alteration phases in the corrosion rind possess colloid dimensions and the flow in the waste package is close to zero, the colloid removal term is simplified to σ, a measure of detachability that is unknown. Hence, this equation may not be suitably extended to repository environments.

5.0 Results and Discussion

5.1 Experimental Observations on Colloids from UO_2

UO_2 solids were exposed to deionized water at 25°C for various times. Unirradiated UO_2 was crushed and sieved to isolate 44-µm to 105-µm-sized particles, washed to remove fines, and then heated in a reducing environment to ensure that the oxygen-to-uranium ratio was 2.000. Samples were characterized by x-ray diffraction (XRD) and scanning electron microscopy (SEM) to verify the absence of precipitated secondary phases.

Unsintered powdered uranium oxide (UO_2) in aerated water reacted rapidly (<24 hours) to form meta-schoepite, which in turn aged to charged micro-crystals. In Figure 5.1, a photograph of a vial containing the altered uranium oxide particles shows visibly large bubbles consisting of a coat of the uranium phase floating on the surface of the water bath. XRD (Scintag PAD V) of the suspension demonstrated that the phase was meta-schoepite. Further examination of the bubbles demonstrated that they contained air that allowed them to float. The bubbles were then extracted from the vial and placed on a microscopy slide for closer examination.

With optical microscopy (Nikon E400 EPI Polarized Light Microscope), the metaschoepite crystallites formed a two-dimensional fractal aggregate at the air/water interface (Figure 5.2a). The open structure of the uranyl oxide hydrate fractal aggregates (i.e., diffusion-limited aggregation), suggested high "sticking probabilities" for the interacting particles. Removal of the air/water interface by placing a cover-slip over the sample destroyed the fractal arrangement. When 1 M NaCl solution was added to the UOH suspension, the particles immediately aggregated along the air-water interface forming a dense flocculated structure (Figure 5.2b). The images were typical of a reaction-limited aggregate. The high ionic strength reduced the interaction potential, causing flocculation, but the bonding to the air-water interface was sufficiently strong to prevent the colloids from completely falling out of the suspension. Under SEM (JEOL JEM840), the particles were found to be extremely fine grained, and the characteristic morphology of schoepite could not be identified (Figure 5.3). The particles at the bottom of the test vessel were always identified as fully hydrate UOH phases. Only the "meta" variety was observed at the air-water interface.

Similar flotation was observed for meta-studtite [$UO_2(O_2)(H_2O)_2$] formed by the reaction of spent fuel with water (McNamara et al. 2002); however, the degree of flotation was not as extensive, which may reflect structural differences between meta-schoepite and meta-studtite.

Figure 5.1. Photograph of Uranyl-Bearing Bubbles Attached to the Air/Water Interface
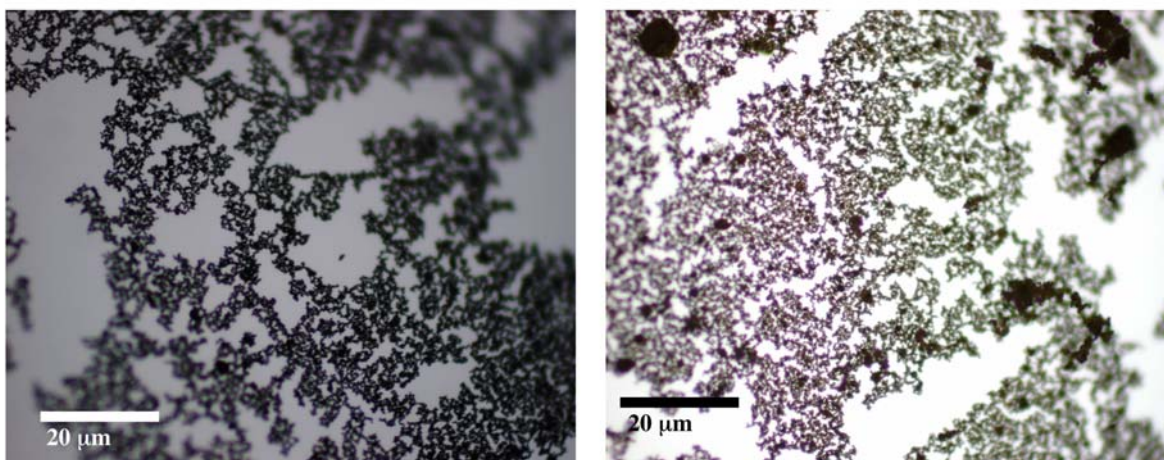
Figure 5.2. Light Microscopy Images of Uranyl Oxide Hydrate (UOH) Particles at the Air-Water Interface Exhibiting
a: Diffusion Limited Aggregate Fractal Structure in deionized water at the air-water interface
b: Reaction Limited Aggregation Behavior in 1 M NaCl Solution at the air-water interface. The UOH particles are in focus in the center of each of the images; as one moves away from the center, these particles go out of focus owing to the curvature of the water film.

40 µm

Figure 5.3. Inverted Contrast Backscattered Electron Scanning Electron Micrograph of Micro-Crystals of Meta-Schoepite with Smaller Fragments of UO₂ Formed During Corrosion of Uranium Oxide

Several surface chemical mechanisms have been proposed to explain the flotation process. A mechanism that fully accounts fo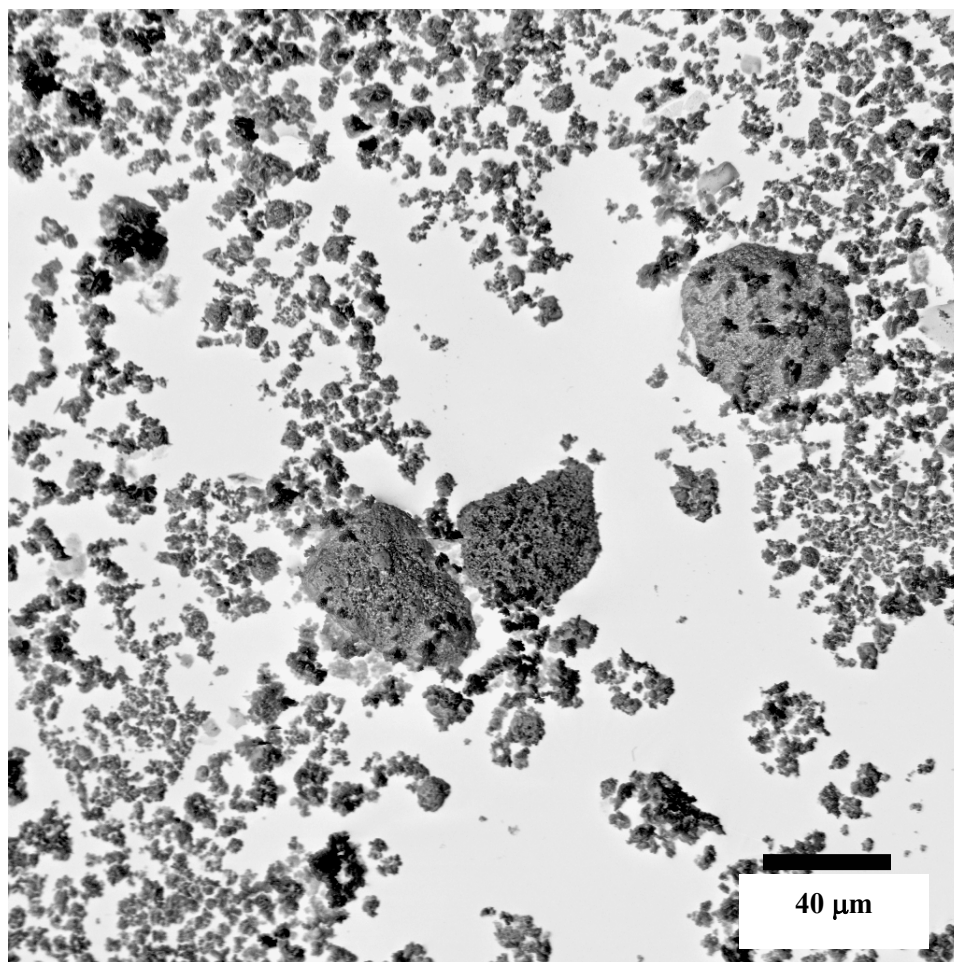r the interaction between a hydrophobic mineral surface and an air bubble is still incomplete. The flotation of meta-schoepite phases is more extensive than for any other heavy metal oxide, including meta-studtite phases. It has been generally accepted that in weak electrolytes, both the air bubble and particle are negatively charged, and both interfaces may be considered to be hydrophobic with high interfacial energy.

Changing the test vessel from an air-water system to an octanol-water system retained the self-organized two-dimensional arrays of particles. The attachment of the uranyl oxide hydrate particles to an octanol/water interface is clear evidence of the hydrophobic nature of the UOH particles. Furthermore, increasing the ionic strength of the water by adding 1 M NaCl or Na_2SO_4 decreased particle-particle distances in the curved plane of the air/water interface, yet retained the bubble structure. The hydrophobicity of the UOH particles increased, as evidenced by a higher contact angle. In these experiments, the UOH particles are behaving according to classical (van der Waals attractive forces) colloidal theory, but only in the curved plane of the air-water interface. The presence of an air-water interface allows the attached UOH particles to move within the interface and results in the generation of

large open fractal aggregates or flocs. These open structures are suggestive of a diffusion-limited structure (i.e., the "sticking potential" is high for these phases). The fractal nature of these particle agglomerates can be seen by viewing the higher magnification SEM image (see Figure 5.3). The image contrast has been inverted so as to allow better comparison with optical images. Some of the structural relationships have been lost through drying on the sample mount; however, the particles exhibit the same random interactions as in the lower magnification optical images. At even higher magnifications with transmission electron microscopy (TEM) (see Figure 5.4), the particles still exhibit a high degree of disordered particle-particle attachment. The particles in the TEM image are clearly colloidal. Some particles are on the order of nanometers in diameter. Distinct euhedral crystallographic forms of the crystalline U(VI) phase, meta-schoepite, were not observed.

Although it is possible that organics below infrared (IR) detection limits may have been present in the samples tested, the degree of flotation in the UO_2 experiments indicates that the flotation process did not involve organic surfactants. A small amount of organic material is present in all starting nuclear fuels as a pellet-forming aid; however, this material is destroyed during sintering.

Meta-schoepite and schoepite are composed of sheets of linked uranyl (VI) ions, with two oxygens bonded axially and shares five oxygens in the equatorial plane (Weller et al. 2000). Meta-schoepite consists of compositionally identical layers to schoepite except for the loss of eight water molecules per unit cell. The removal of water from schoepite results in only slight modification to lattice parameters **a** and **b** and only a 2.8% contraction in the **c**-axis. However, it is precisely because there is little change in the unit cell volume that the change in surface charge density may be so significant. The increased surface charge density would result in a stronger electrostatic force holding these phases to the negative air/water interface. This is the only way to explain why the metaschopeite "floats" whereas schoepite does not "float" under the tested conditions. This difference also supports that the flotation process does not involve an organic surfactant. In Figure 5.5, we have proposed a possible model for meta-schoepite colloid attachment to a non-polar interface based on knowledge of the meta-schoepite structures; however, there is no conclusive evidence for this from microscopy observations. Distinctive meta-schoepite crystals were not found. The force attaching the UOH particles to the interface is sufficient to allow large colloid fractal aggregates or flocs to remain stable over a range of pH.

The structure of studtite $[(UO_2)(O_2)(H_2O)_2](H_2O)_2$ has recently been elucidated by Burns and Hughes (2003). Studtite is composed of uranyl polyhedral chains. This is not like most uranyl oxide hydrate minerals that are based upon sheets of uranyl polyhedra, which have low-valence cations and H_2O groups located between the sheets. Meta-studtite is thought to consist of the same chains of uranyl polyhedra as studtite but with H_2O bonded to uranium. Burns and Hughes indicate that published unit cell parameters for meta-studtite may be in error; therefore, it is not possible to comment on the probable change in surface charge density between studtite and meta-studtite at this point. However, these structural differences may explain why the coated bubble structure observed with meta-schoepite was not observed with meta-studtite.

a — Uraninite particles

Meta-schoepite

50 nm

b — SAED

[001]

[100]
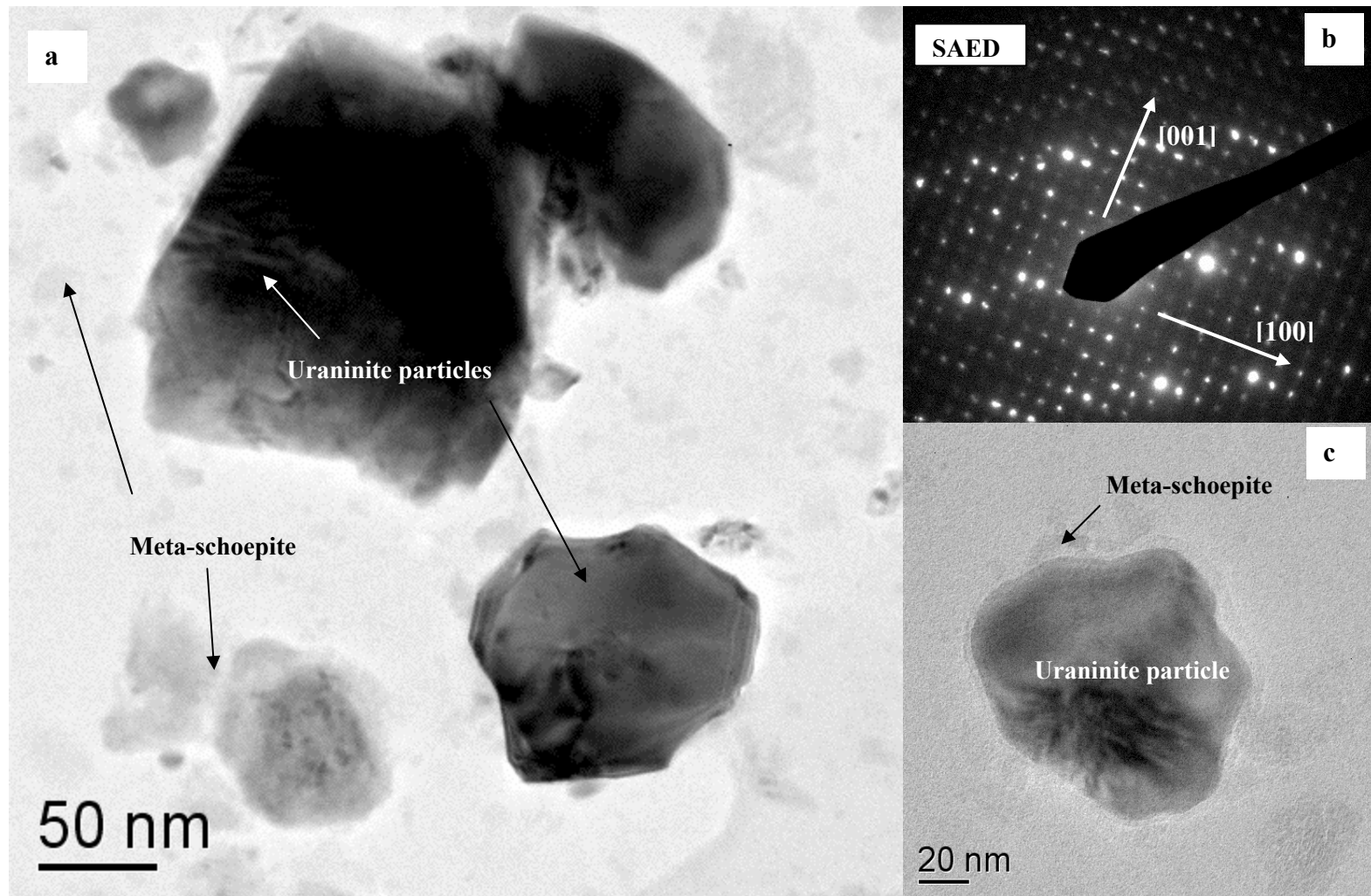
c — Meta-schoepite

Uraninite particle

20 nm

5.5

Figure 5.4. **(a) Transmission Electron Microscopy Image of Colloidal Uranly Oxide Hydrate and Uraninite Particles; (b) Electron Diffraction Pattern of Meta-Schoepite taken along B[010]; (c) High Magnification Image of Coated Uraninite Particle**

The stabilization of UO_2-derived alteration phases at air/water interfaces may have significant implications for possible future immobilization of CSNF corrosion products. If the charged UOH particles can trap fragments of fuel, as they do with UO_2 particles, effective solubility values for all fission- and neutron-capture products in SNF may be different from current predictions under unsaturated conditions. However, if fully saturated conditions at Yucca Mountain are assumed, this might exacerbate radionuclide release. Given the high degree of hydrophobicity in the alteration products from CSNF and UO_2, the role of air-water interfaces in the waste-form colloid generation model should not be ignored because of the potential benefit to performance assessment.
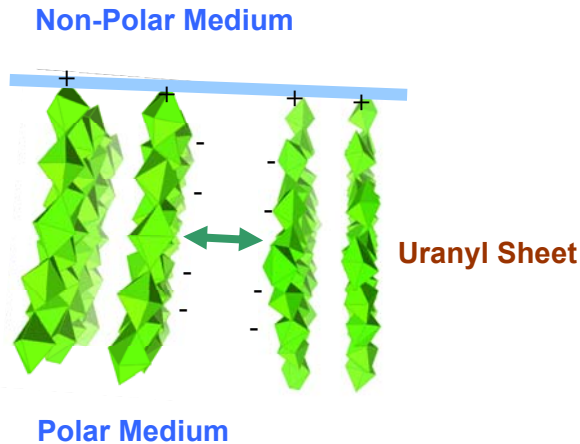

Figure 5.5. Possible Theoretical Schematic Diagram of the Polyhedral Model of the Uranyl Oxide Hydrate Sheet Structure Attached to a Polar/Non-Polar Interface Through Positive Edge Charges and Attraction to Similar Particles by van der Waals Forces (arrow)

5.2 Flotation in Heavy Metal Oxides

Hydrophobicity is also exhibited by a number of heavy oxide minerals, including thorium oxide, tungsten oxides, and plutonium oxides. Experiments were performed on the capability for these oxides to attach to air-water interfaces. Data are presented from experiments on tungsten and thorium oxides.

5.2.1 Tungsten Oxide Colloids

A high-resolution image of a floating tungsten oxide is shown in Figure 5.6. There were no signs of corrosion products similar to the uranyl oxide hydrates, and the tungsten solid did not exhibit the same degree of hydrophobicity as the uranyl phases; however, particles were clearly observed at the air-water interface.
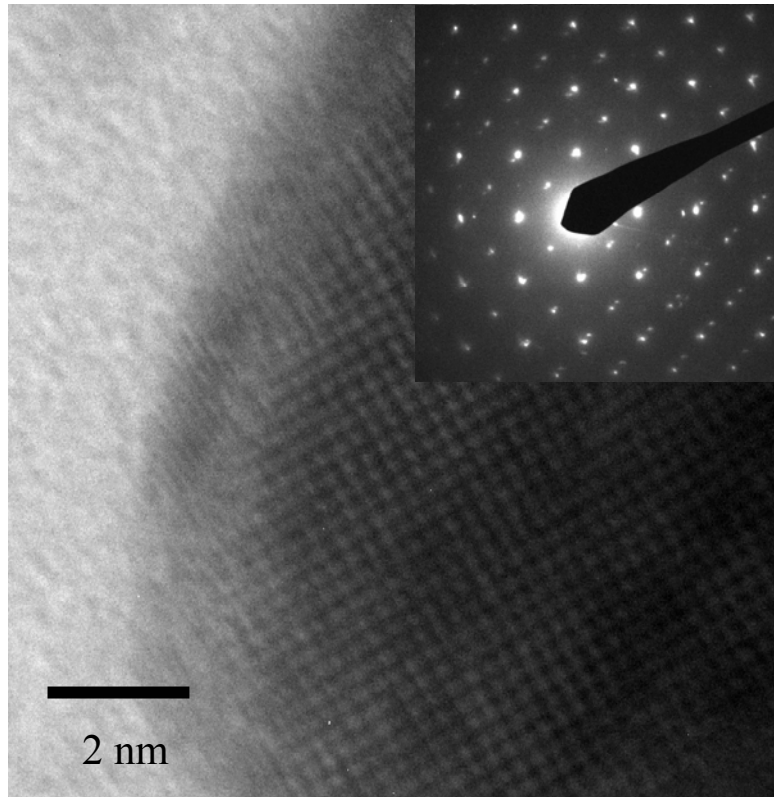
Figure 5.6. Transmission Electron Micrograph of Tungsten Oxide and Selected Area Electron Diffraction Pattern of the Solid

5.2.2 Thorium Oxide Colloids

A small quantity of ThO_2 was placed in a water-filled vial. The oxide was left for several weeks before being examined. There was evidence of some flotation of the oxide; however, this was not as extensive as that observed with meta-schoepite. Under the optical microscope, square particles of ThO_2 were visible around 1 to 2 μm in size. Images of the thorium oxides particles are shown in Figure 5.7. The reasons for flotation of thorium oxide are unclear as this phase should not form an alteration layer and does not possess the platy texture like tungsten oxides or uranium (VI) oxide hydrates.
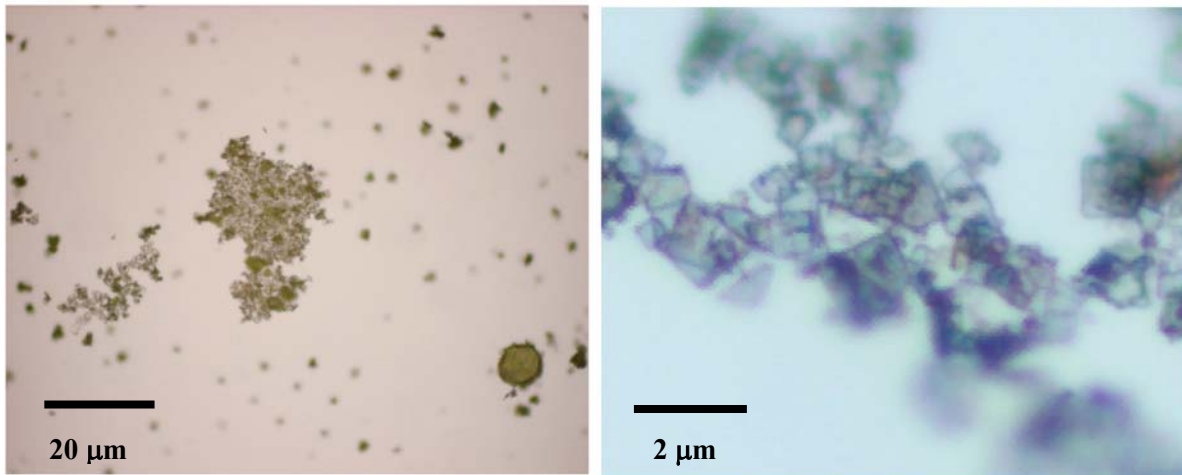
Figure 5.7. Optical Images of Thorium Oxide Particles

5.2.3 Plutonium Oxides

No experiments have been conducted with plutonium oxides to date; however, there are indications that plutonium oxides may be subject to the same effects under some conditions. Rapid precipitation of plutonium oxide from an acidic plutonium nitrate solution can result in the formation of colloidal-sized plutonium oxides that have the potential to become attached to air bubbles. This process has been observed at the Plutonium Finishing Plant at Hanford, but it is unlikely that this type of process would be expected to occur in a repository environment. Nevertheless, it demonstrates that hydrophobicity of metal oxides is common and needs to be accounted for when considering colloid mobility (or lack therein of) in a waste package.

6.0 Colloid Detachment Predictions

The studies reported in Section 5.1 on UO_2 under fully saturated aerated conditions demonstrate that colloids will form rapidly. The static environment of these tests would appear to invalidate the argument that colloid release can be affected by flow. The particles from UO_2 alteration are particularly susceptible to colloid formation owing to their inherent hydrophobicity and propensity to become attached to air-water interfaces (bubbles). Under unsaturated conditions where only thin-films of water are contacting the surfaces of the waste forms, colloid transport (detachment from the surface) will be retarded; however, under saturated conditions, thin-film straining will not occur.

Clay colloid formation from static and dynamic tests on DHLWG occurs via both condensation of release glass elements in solution and by spallation of previously precipitated smectite clay particles from the altered surface. The propensity for smectite clay colloids to condense increases with increasing glass reaction rate. The testing of DHLWG under Product Consistency Test (Method B) can lead to high concentrations of glass elements in solution (Ebert 1995). This type of testing approach may exaggerate predictions for colloid concentrations. The mechanism of colloid formation in spent fuel and UO_2 systems is quite different to that of DHLWG in both saturated and unsaturated conditions owing to inherent differences in the nature of the colloidal alteration products.

Numerically accurate calculation of simultaneous advection, dispersion, thin-film attenuation, and attachment to air-water interfaces will be necessary for the development of the alternative model proposed in this report. A possible numerical solution to Equation 4.4 was obtained in Microsoft Excel 2000 using the iterative option to avoid the issue of circular references. In the numerical approximation reported here, an effort was made to obtain the most stable solution by using the Crank-Nicholson form for the dispersion term in the solution (Gvirtzman and Garfunkel 1996).

$$C_i^{n+1} = \frac{\{C_i^n + \frac{\Delta t q A_L}{\Theta \Delta x^2}[(1-\alpha)(C_{i-1}^n - 2C_i^n + C_{i+1}^n) + \alpha(C_{i-1}^{n+1} - 2C_i^{n+1} + C_{i+1}^{n+1})]\}}{(1 + \frac{2\alpha \Delta t q A_L}{\Theta \Delta x^2})} \tag{6.1}$$

where Θ, q and A_L are the same as in Section 4.0, and $\alpha = 0.5$ (Crank-Nicholson approximation) (Gvirtzman and Garfunkel 1996). Instead of using the explicit finite approximation for the dispersion term, the Lax-Wendroff method as described by McDonald (2003) was used that significantly reduced numerical dispersion in the results. The expression has an additional term from a Taylor series expansion for stability:

$$C_i^{n+1} = C_i^n - \frac{q}{\Theta}\frac{\Delta t}{\Delta x}(C_{i+1}^n - C_{i-1}^n) + \left(\frac{q}{\Theta}\right)^2 \frac{\Delta t^2}{2\Delta x^2}(C_{i+1}^n - 2C_i^n + C_{i-1}^n) \tag{6.2}$$

The graph in Figure 6.1 demonstrates the effect of colloid attachment to air-water interfaces. As k_1 and k_2 increase, colloid retention becomes significant. By understanding the magnitude of these parameters for

colloids from spent fuel, it would be possible to extract more accurate assessments for colloid concentrations in the waste package.

Breakthough Curves
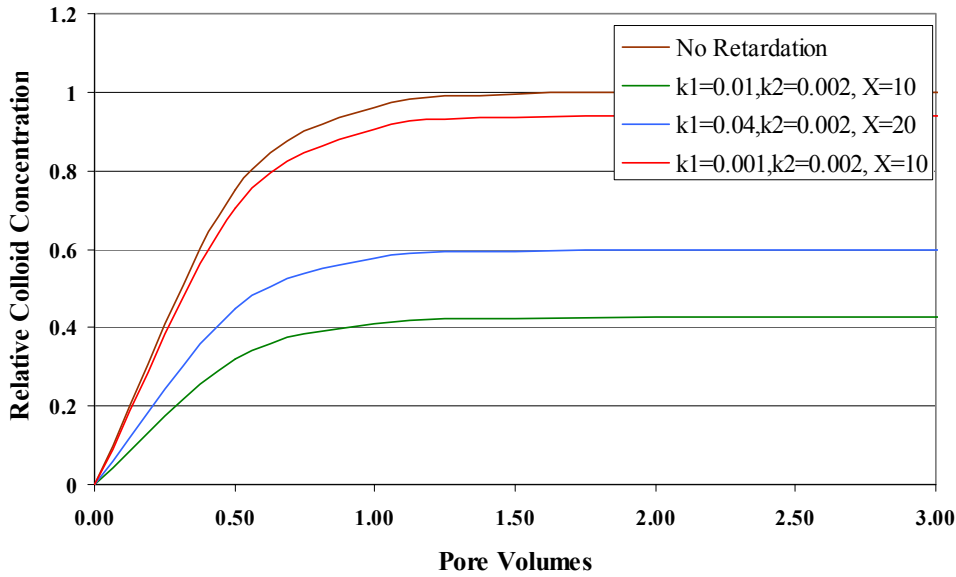
Figure 6.1. Examples of Colloid Breakthrough Curves Demonstrating the Effect of the Colloid Deposition Coefficient on Colloid Concentrations. The results are similar to those reported by Corapcioglu and Choi (1996) and Lenhart and Saiers (2002).

As the immobilization rates increase for the colloids, colloid breakthrough is curtailed. The model assumes irreversible attachment of particles at air-water interfaces. As these curves use pore volumes, the effect of flow rate is not considered.

7.0 Conclusions

Hydrophobic uranyl oxide hydrate (meta-schoepite) colloids derived from spent-fuel corrosion may be thermodynamically stable when attached to an air-water interface and could be irreversibly held by surface tension. It is likely that meta-schoepite is immobilized more effectively than any other heavy metal oxide, including meta-studtite, because of structural peculiarities. It is likely that plutonium colloids will become attached to the uranyl oxide hydrate particles and immobilized on the large surface area of these phases. Chemical factors (pH and ionic strength) alone have not been capable of predicting colloid concentrations in natural aquifers, and these factors are unlikely to be effective in predicting colloid concentrations from altered waste forms within the proposed Yucca Mountain Repository environment. The complicated nature of the parent materials and their interaction with saturated and unsaturated water add to the complexity. However, as McDowell-Boyer (1992) argues, unless the colloidal system is subject to physical and chemical alteration, colloid release will not occur. To mobilize colloids, the critical shear stress, or activation energy for release, must be overcome. Classic DLVO theory does not account for this effect and may over predict colloid concentrations. Observations in natural systems suggest that colloid release is most prevalent under extreme conditions that are unlikely to occur in the Yucca Mountain Repository waste packages. The Lenhart and Saiers (2002) theory suggests that the volumetric air content in the waste package during corrosion will allow us to determine the range of colloid thin-film straining (or colloid immobilization). It is unclear whether the Kozeny-Carman relationship (Govindaraju et al. 1995) or the equation presented by Ryan and Gschwend (1994) would permit estimation of particle removal without the aid of experimental determination of CSNF colloid detachability with anticipated low flow rates. However, by establishing the extreme conditions that result in colloid mobilization from altered CSNF waste forms, it will be possible to bound the impact of colloids on colloid-facilitated radionuclide transport within the proposed Yucca Mountain Repository.

8.0   References

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