

POTENTIAL IMPLICATIONS OF COLLOIDS ON THE LONG-TERM PERFORMANCE OF A HIGH-LEVEL RADIOACTIVE WASTE REPOSITORY

Prepared for

**Nuclear Regulatory Commission
Contract NRC-02-93-005**

Prepared by

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

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PREVIOUS REPORTS IN SERIES

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ABSTRACT

The report discusses technical considerations related to the role of colloids in the release of radionuclides from vitrified wastefoms and spent fuel and their potential impact on the performance of a geologic high-level radioactive waste (HLW) repository. Topics covered include Nuclear Regulatory Commission (NRC) regulatory requirements related to radionuclide release; U.S. Environmental Protection Agency (EPA) radionuclide release limits; key technical uncertainties (KTUs); Yucca Mountain geology and geochemistry; and colloid behavior related to nucleation (generation), stability, sorption, and transport in a geologic medium. A review and discussion of models related to nucleation, growth, and transport of colloids are provided. A comprehensive list of literature references is provided to facilitate in depth examination by interested readers of the topics discussed in this report.

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ABBREVIATIONS AND ACRONYMS

CNWRA	Center for Nuclear Waste Regulatory Analyses
CDS	Compliance Determination Strategy
DOC	dissolved organic carbon
DOE	U.S. Department of Energy
DWM	Division of Waste Management
EBS	engineered barrier system
EDL	electrostatic double layer
EDTA	ethylenediaminetetraacetic acid
EM	emission spectroscopy
EPA	U.S. Environmental Protection Agency
FCRG	Format and Content for the License Application for the High-Level Waste Repository
HLW	high-level [radioactive] waste
KTU	key technical uncertainty
LANL	Los Alamos National Laboratory
LARP	License Application Review Plan
MW	molecular weight
NMSS	Office of Nuclear Material Safety and Safeguards
NRC	Nuclear Regulatory Commission
NTS	Nevada Test Site
PA	performance assessment
pH _{ZPC}	pH value at the zero point of charge
R _f	retardation factor
SA	surface area
SEM	scanning electron microscopy
SWL	static water level
TDS	total dissolved solids
TOC	total organic carbon
ZPC	zero point of charge

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QUALITY OF DATA

DATA: Sources of data are referenced in each chapter. The respective sources of these data should be consulted for determining their levels of quality assurance.

EXECUTIVE SUMMARY

Recent publications have suggested that long-lived radionuclides (actinides) may be released from high-level radioactive waste (HLW) (vitrified wastefoms and spent nuclear fuels) to aqueous solutions in the form of microscopic particles called colloids. Performance assessment (PA) models developed for the geologic disposal of HLW, however, generally consider only the transport of dissolved species. If significant amounts of radionuclides can be released from the HLW in the form of colloids, these models may need to be modified to include colloid transport processes. Although the demonstration of compliance with the requirements of the Code of Federal Regulations, Title 10, Part 60 (10 CFR Part 60) is incumbent upon the applicant, this report was undertaken as a joint project by the Center for Nuclear Waste Regulatory Analyses (CNWRA) and the Nuclear Regulatory Commission (NRC) to provide information related to colloids, their potential role in the release of radionuclides from the wasteform, and the transport of radionuclides through the geologic system. This report is considered a *first step* in providing the basis for prelicensing guidance to the U.S. Department of Energy (DOE), identification of regulatory issues and compliance concerns, and development of a technical data and information base to aid in the review of the license application by NRC. It is based on a review and examination of literature related to the formation and transport of colloids in suspension through geologic media that is potentially applicable to HLW geologic disposal.

The requirements in the NRC regulation (10 CFR Part 60) for HLW disposal during the post-containment period and the U.S. Environmental Protection Agency (EPA) requirements (40 CFR Part 191)¹ related to cumulative releases of various radionuclides over the 10,000-yr post-closure period are summarized. Based on the analysis of the NRC regulation, a number of technical uncertainties related to HLW disposal at the Yucca Mountain site have been previously identified by NRC and CNWRA staff as part of the License Application Review Plan (LARP). Ten technical considerations, called key technical uncertainties (KTUs), are identified and discussed relative to specific aspects of 10 CFR Part 60. These uncertainties are related to: (i) the ability to project the nature and rates of Quaternary geochemical processes, (ii) the identification of geochemical conditions that would inhibit particulate and colloid formation, (iii) the characterization of the geochemistry of the partially saturated hydrologic zone, (iv) the effects of degree of saturation on geochemical processes, such as colloid formation and sorption, on the transport of radionuclides, (v) the parametric representation of retardation processes, (vi) the identification of processes adversely affecting the engineered barrier system (EBS), (viii) the magnitude of the effects of geochemical processes on radionuclide retardation, (ix) the identification of potentially adverse effects of geochemical processes on the EBS performance, and (x) the ability to predict release of radionuclides from waste packages.

Colloids are differentiated from molecules and larger particles on a size basis (e.g., colloids refer to particles in the size range of 10^{-8} to 10^{-15} m). Colloids is not a classification based on chemical composition or on radionuclide content; however, the HLW literature has adopted a terminology convention to differentiate between the possible various types of radionuclide-bearing colloids, namely, (i) groundwater colloids, (ii) real or true colloids, and (iii) pseudocolloids. Groundwater colloids are naturally occurring in all groundwaters; real or true colloids are produced by the aggregation of hydrolyzed actinide ions, and pseudocolloids are distinctively different from one another in their chemical properties. Groundwater samples collected in Nevada show colloid concentrations to be in the

¹ 40 CFR Part 191 was remanded by the Courts. The technical bases for HLW standards are being reviewed by the National Academy of Science.

0.27–1.35-mg · L⁻¹ range, and the colloid size to be in the 1.0–0.03-μm range. A surprising and significant conclusion of the study was that no connection between colloid concentration and sample environment was detected (with the exception of a few outliers). This conclusion was based on comparison of data from three sets of geologic conditions: (i) carbonate versus volcanic sources, (ii) well versus spring, and (iii) on and off the nuclear weapons test site.

Field evidence for colloids and the potential influence of natural systems on sorption, filtration, and transport of colloids from HLW repository sites around the world are summarized in the report. It is concluded that in addition to natural colloids, several of the radionuclides predicted to be important in the repository performance are known to form true or real radiocolloids through hydrolysis, polymerization, and crystallization. Both Am and Pu exhibit appreciable colloidal formation at high pH, possibly on Am(OH)₃ and Pu(OH)₄, respectively. In contrast, negligible fraction of Np is released in colloidal form, except at pH > 10. In several studies no colloid formation of radionuclides in synthetic brines down to particle sizes of 15 nm has been reported. This lack of colloid formation is explained on the basis of inhibited (or suppressed) hydrolysis in high-ionic strength solutions.

The potential sources of colloids in the repository environment are naturally occurring groundwater colloids, engineered barrier system (EBS) (waste package and backfill) corrosion products, vitrified wasteforms and spent fuel, and precipitation processes aided by the repository-area thermal gradient. The complex nature of the mechanism of colloid formation leads to uncertainties in the interpretation of experimental results. The migration of radionuclides is based on generation and transport of colloids formed mainly due to the condensation and dispersion processes. In the context of HLW disposal, colloids may only be significant to the extent to which they influence radionuclide transport through the geologic setting. A review of previous studies on sorption, filtration, and transport of colloids is provided. The emphasis is on actinides of interest to the long-term performance of a geologic repository, such as Am, Np, and Pu. Data from true or real and pseudocolloids in a number of different groundwaters are examined. Sources of colloids are discussed in the context of their sorption, filtration, and release in the near field, and their transport to the far field of the repository. To have an adverse effect on repository performance, colloids formed from spent fuel must migrate from the near field through the EBS to the far field. The concentrations of dissolved radionuclides are expected to be dilute in the far field. Under these circumstances, colloids could become a significant source of radionuclides in the far field.

Concern has been expressed regarding the possibility of introducing significant amounts of man-made materials in the repository that may lead to either the formation or mobilization of radioactivity in colloidal or particulate form. Estimates and data related to only a small number of activities at the Yucca Mountain repository site show that large amounts and several types of materials (both organic and inorganic) will be used during the construction phase of the repository. The types of materials being used and the quantities of these materials could influence the production of pseudocolloids. For example, for one exploratory shaft portal facility, the quantity of human-introduced material that will be introduced in 1 yr is estimated to be 26,000,000 gal. of water, 250,000 gal. of diesel fuel, 10,000 lb. of rockbolt resin, 1,800 sq ft of extruded polystyrene, 50 cu yd of bentonite clay, and 250 gal. of cable lubricant. A significant amount of these materials is expected to be left behind and will be sealed upon permanent closure of the repository.

A review of current literature on colloid transport models is provided. The mathematical treatment of colloid transport under geologic conditions is also discussed. The early modeling efforts led to the development of simple models of colloid transport in a single fracture. It is concluded that despite the

studies related to colloid transport at waste disposal sites, a model for colloid transport adequate for use in PA calculations applicable to HLW disposal in partially saturated media is still lacking.

1 INTRODUCTION

The relevant literature pertaining to the behavior of colloids in the context of a high-level radioactive waste (HLW) repository setting was reviewed and examined. This report identifies properties of colloids that are likely to influence the migration of radionuclides in a repository environment. This study also identified and, to the extent practicable, assessed the importance of colloid-related behavior on the performance of the HLW repository during the post-containment period. The results of the study will be the foundation for deciding (i) if colloids present a possible mechanism for the fast release of radionuclides to the accessible environment, and (ii) what studies or investigations should be conducted to resolve key technical uncertainties (KTUs) in the regulatory requirements related to colloid formation and transport. This report will also provide bases for future Nuclear Regulatory Commission (NRC) work in the area of colloids, including that work related to performance assessment (PA) and compliance determination methods (CDMs).

Colloid systems may be defined as systems containing at least two components: (i) a continuous dispersing medium, and (ii) a dispersed phase. The classical description of a colloidal system is one that is composed of dispersed-phase particles in the range of 1- to 1,000-nm-diameter size in another homogeneous phase (usually a liquid). Particles smaller than 1 nm do not exist as a discrete phase, and, therefore, any system containing such small particles cannot be considered as heterogeneous. Figure 1-1 shows the general range of the size spectra of water-borne particles including colloids (McCarthy and Zachara, 1989). The chemical composition, shape, structure, and the size of colloids vary widely, depending on the geochemical system. The colloid particle concentration is also highly variable [e.g., a range of 10^8 to 10^{17} colloidal particles per liter has been reported for groundwaters (Kim, 1991)]. Because of their very small size and due to their high surface area to mass ratio, colloids have some peculiar properties (e.g., colloid systems characteristically undergo fast reactions such as sorption, ion exchange, and dispersion).

Evidence has demonstrated that colloids can be formed and released from HLW (Ahn, 1993; Avogadro and Lanza, 1982; Bates et al., 1992a; Ebert and Bates, 1992; Manaktala, 1992, 1993; Manaktala et al., 1993, 1994; Smith, 1993a; van der Lee et al., 1993). However, it is not clear if colloids can *a priori* be considered to have adverse or beneficial effects on release and transport of radioactivity with respect to the requirements in the regulation for HLW disposal promulgated by the NRC, namely the Code of Federal Regulations, Title 10, Part 60 (10 CFR Part 60). Current PA calculations assume that the mobile concentrations of most sparingly soluble radionuclides in any groundwater that contacts the waste will be "solubility limited" (Apted and Engel, 1990; O'Connell, 1990). An important implicit assumption in this solubility-limited approach is that colloids are not formed or that they play an insignificant role in radionuclide release. However, literature references that show that the release of some low-solubility actinides (e.g., Pu and Am) from vitrified wastefroms occurs predominantly via colloids (in some cases, nearly 100 percent) (Bates et al., 1992b).

The results of a recent study on vitrified wastefroms, using a simulated unsaturated repository environment, indicate that 70 percent of the Np can be considered truly dissolved. On the other hand, greater than 99 percent of the Am and Pu were retained as colloidal particles (Bates et al., 1992a). It was also found that, in general, the ratio of radioactivity of the filtered to the dissolved fraction was greater than 1,000:1 for the radionuclides studied (Bates et al., 1992a). In a field study at Los Alamos, New Mexico, Pu and Am were detected in monitoring wells over a kilometer from the inferred point of source; the transported radionuclides were characterized as being bound on colloids in the 25- to 450-nm

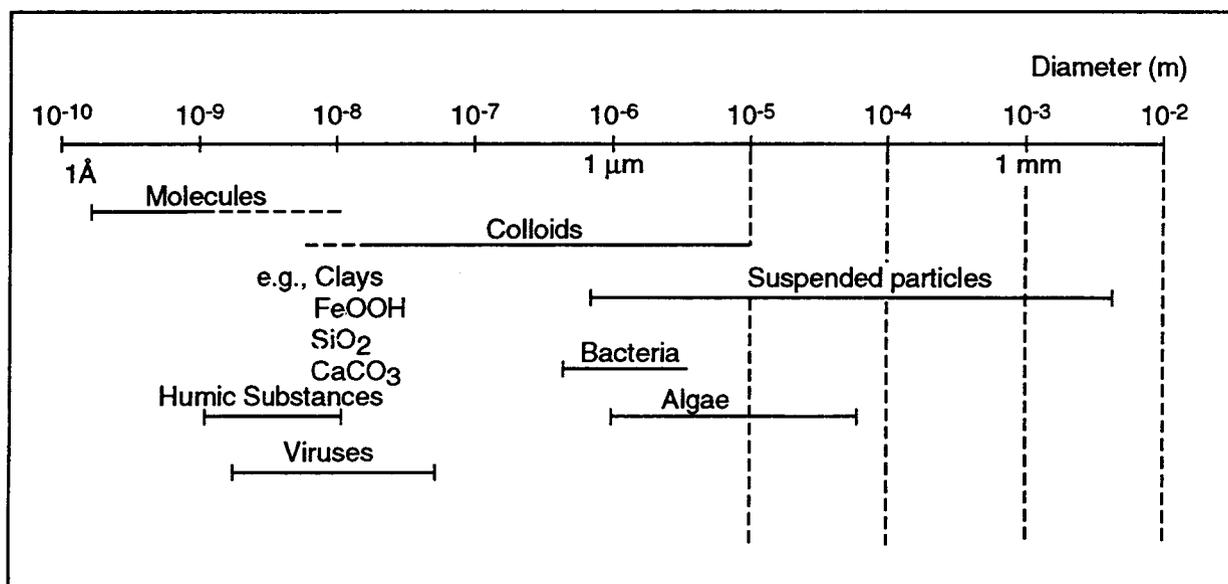


Figure 1-1. Size spectrum of waterborne particles (after McCarthy and Zachara, 1989)

size range (Nelson and Orlandini, 1986). Another comprehensive study on the chemical behavior of transuranic elements in aqueous systems concluded that failure to account for colloid transport as a carrier of actinides can lead to serious underestimates of the actinide migration (Kim, 1993). The results of such studies lead one to conclude that repository performance models, which assume maximum release of actinides to be limited by the solubility limit in groundwaters, particularly for Pu, Am, and Cm isotopes, could significantly underestimate the potential for radionuclide release into the environment. In the context of the post-closure requirements in 10 CFR Part 60, there is concern that enhanced transport mechanisms due to releases in colloidal form could lead to an increase in the radioactivity beyond the permissible limit during the 10,000-yr regulatory period following permanent closure of the repository.

This report provides a literature review of topics pertinent to the potential impact of colloids on the release of radionuclides in a HLW repository environment. This information can be used to address KTUs in the regulatory requirements related to colloid formation and transport. Applicability of current data to PA needs can be used to identify KTUs that require further investigation. The report concludes with recommendations. This report should be considered as a *first step* toward developing a plan for resolving concerns and technical considerations related to the role of colloids in the release and transport of radionuclides and in providing U.S. Department of Energy (DOE) precicensing guidance. Identification of regulatory compliance issues and development of a technical data and information base will aid in the review of the repository license application by the NRC.

1.1 REGULATIONS APPLICABLE TO HIGH-LEVEL WASTE DISPOSAL AND REPOSITORY PERFORMANCE

This section discusses the regulatory requirements related to the geologic disposal of vitrified (glass) HLW and spent fuel in the United States. The discussion covers both the NRC requirements

related to containment and gradual release rate of radionuclides and the U.S. Environmental Protection Agency (EPA) requirements related to the cumulative release of radionuclides over 10,000 yr following repository closure.

1.1.1 Nuclear Regulatory Commission Regulations

The regulations regarding the siting, operation, and construction of a HLW geologic repository are contained in 10 CFR Part 60. The siting criteria containing conditions favorable to waste disposal in a geologic repository and potentially adverse conditions are given in 10 CFR 60.122(b) and 122(c), respectively. As part of the license application, the presence or absence of these conditions is to be demonstrated by the DOE site characterization program. The impact of these conditions is to be addressed in PA calculations to assess the performance of the particular barriers after permanent closure (10 CFR 60.113) and to determine if the overall system performance objective is met for the geologic repository after permanent closure (10 CFR 60.112).

The results of the site characterization studies will be included in the Safety Analysis Report (SAR) submitted with the license application. If favorable conditions are demonstrated to be present, they are to be factored into the PA with the engineered barrier system (EBS) to provide assurance that the repository will meet performance objectives related to waste isolation. The lack of a favorable condition is not used as criteria for disqualification of a potential site. Potentially adverse conditions may compromise the ability of the repository to isolate waste. If one or more potentially adverse conditions are present, PA calculations must incorporate the condition(s) to evaluate if the repository can meet performance objectives. If adverse conditions are present at the site, combinations of favorable conditions may offset the effect of one or more potentially adverse conditions. This possibility should also be incorporated into PA.

In 10 CFR 60.113, the performance requirements for the EBS and geologic setting subsystems of the repository system are stipulated in 10 CFR 60.113(a)(1). These performance requirements consist of two parts: (i) a containment requirement for the HLW packages, and (ii) a radionuclide release rate limit from the EBS. Taken together, these two parts are intended to control the release of radioactive materials to the geologic setting [10 CFR 60.113(a)(2)] and to add confidence that the overall system performance objectives for the repository (i.e., 10 CFR 60.112) will be met. The calculated total release limit to the geologic setting is limited to 1 part in 100,000 per yr of the total inventory that remains after 1,000 yr of radioactive decay. In the multiple barrier concept, the geologic setting is to provide additional protection against radionuclide migration in the subsurface. The performance of the geologic setting is measured against minimum groundwater travel time from the repository disturbed zone to the accessible environment. As described in 10 CFR 60.112(a)(2), travel time along the fastest path for radionuclide migration to the accessible environment is to be more than 1,000 yr.

In 10 CFR 60.112, the performance requirements for the overall geologic repository system are provided. These requirements incorporated, by reference, any regulation promulgated by the EPA for the disposal of HLW.

Although the requirement in the rule for limited release from the EBS in the post-containment period is clearly stated in numerical terms, the companion or associated requirement for "substantially complete containment" during the containment period is qualitative and subject to interpretation

(Manaktala and Interrante, 1990). The technical concerns expressed and the discussions in this report are related to the post-containment release part of the regulations.

1.1.2 U.S. Environmental Protection Agency Standard

The total activity of the various radionuclides present in HLW is only part of the measure of their importance. In addition to the NRC requirements of containment of radioactivity and the gradual release over the 10,000-yr period of regulatory interest, the repository also has to meet the cumulative radionuclide release requirements set by the EPA. The EPA standard that limits the release of radionuclides to the environment for 10,000 yr after disposal is given in 40 CFR Part 191 (U.S. Environmental Protection Agency, 1992)². Table 1-1 (U.S. Environmental Protection Agency, 1992) lists the release limits for various radioactive isotopes. Other sections of 40 CFR Part 191 applicable to individual protection, groundwater protection, etc. could also be impacted by colloids. As such, they also need to be addressed in a repository license application.

Radionuclide release, as discussed in this report, would take place only as a result of intrusion of water into the repository (except for gaseous release, such as $^{14}\text{CO}_2$, which is not covered in this report). The time of failure of the waste package and the repository environment would determine the radionuclide inventory available for release and the near-field environment that, in turn, will affect the generation and transport of radionuclides in solution or colloidal form. For the Yucca Mountain site, considerable uncertainties exist as to when the waste packages may be contacted by liquid water, as well as uncertainties in the geochemical environment of the waste package. The uncertainties arise from the changing status of the waste package materials selection, waste package design (including thermal loading), and limited site geological data. In time, additional information and data are expected to be available in these areas, thereby enabling, better prediction of the contact time of groundwaters with the HLW and also the quantity and chemical composition of water that may contact the HLW. The accuracy of the overall system performance estimates would depend on reducing or eliminating these uncertainties.

1.1.3 Relative Importance of Radionuclides in the High-Level Waste

Radionuclides important for the long-term geologic repository will be site-specific (e.g., controlled by repository environment and transport mechanisms), and will also depend on time scales, regulations, and waste types. The time frame for regulatory interest can be divided into two regimes: (i) the containment period, and (ii) the post-containment period. This report deals with the post-containment period in which colloids could be generated and transported.

Radionuclides and their anticipated contribution to the total inventory for spent fuel and vitrified wasteform are shown in Tables 1-2 and 1-3. The data in these tables show the fractional contribution to the inventory of radionuclides at 10^2 , 10^3 , 10^4 , and 10^5 yr after disposal. The radionuclide ^{14}C is produced mainly from activation of ^{14}N , which is present in both fuel and cladding as a production or processing impurity. The ^{14}C content in vitrified wasteforms is considered insignificant compared to its inventory in spent fuel and cladding. The fission product ^{129}I is important, but is not shown in the tables because its contribution to the total inventory is small.

² 40 CFR Part 191 was remanded by the Courts. The technical bases for HLW standards are being reviewed by the National Academy of Science.

Table 1-1. Limits for cumulative releases to the accessible environment for 10,000 yr after disposal (adapted from U.S. Environmental Protection Agency, 1992)

Radionuclide	Release limit per 1,000 MTHM* or other unit of waste (curies)
Americium-241 or -243	100
Carbon-14	100
Cesium-135 or -137	1,000
Iodine-129	100
Neptunium-237	100
Plutonium-238, -239, -240, or -242	100
Radium-226	100
Strontium-90	1,000
Technetium-99	10,000
Thorium-230 or -232	100
Tin-126	1,000
Uranium-233, -234, -235, -236, or -238	100
Any other alpha-emitting radionuclide with a half-life greater than 20 yr	100
Any other radionuclide with a half-life greater than 20 yr that does not emit alpha particles	1,000
* MTHM=Metric Ton Heavy Metal	

Early in the containment period, two elements with short-lived isotopes, namely, ^{90}Sr and ^{137}Cs , provide a major contribution to the radionuclide inventory. However, the waste package is designed to provide containment of the HLW for the first 300 to 1,000 yr after disposal (10 CFR Part 60). Therefore, under the expected conditions, these two short-lived radionuclides would decay to insignificant levels during the containment period (i.e., they are assumed to be not subject to release). At the beginning of the post-containment period, the actinides are the predominant radionuclides. Because of the much higher concentration of radionuclides in spent fuel than in vitrified wasteform, spent fuel is likely to contribute a proportionately much larger fractional release of radionuclides to the repository environment.

Table 1-2. Primary radionuclides contributing to repository inventory for pressurized water reactor (PWR) spent fuel with burnup of 33,000 MWd · MTHM⁻¹ (adapted from Kerrisk, 1985)

Radionuclide and Percent of Total Activity for Various Decay Times							
10 ² yr		10 ³ yr		10 ⁴ yr		10 ⁵ yr	
¹³⁷ Cs	25%	²⁴¹ Am	51%	²³⁹ Pu	51%	²³⁹ Pu	33%
¹³⁷ Ba	24% ^a	²⁴⁰ Pu	27%	²⁴⁰ Pu	39%	⁹⁹ Tc	17%
⁹⁰ Sr	17%	²³⁹ Pu	17%	⁹⁹ Tc	3%	⁵⁹ Ni	4%
⁹⁰ Y	17% ^b	²⁴³ Am	0.9%	²⁴³ Am	1%	⁹³ Zr	3%
²⁴¹ Am	9%	²³⁹ Np	0.9% ^c	²³⁹ Np	1% ^c	^{93m} Nb	3% ^d
²³⁸ Pu	3%	⁹⁹ Tc	0.7%	⁵⁹ Ni	1%	²³⁴ U	3%
²⁴¹ Pu	2%	⁵⁹ Ni	0.3%	²³⁴ U	0.4%	²⁴² Pu	3%
²⁴⁰ Cm	1%	²³⁴ U	0.1%	⁹³ Zr	0.4%	²³⁷ Np	2%
²³⁹ Pu	0.8%	⁹³ Zr	0.1%	^{93m} Nb	0.4% ^d	²³³ Pa	2% ^e
⁶³ Ni	0.8%	^{93m} Nb	0.1% ^d	²⁴² Pu	0.4%	²²⁶ Ra	2% ^f
¹⁵¹ Sm	0.4%	²⁴² Pu	0.1%	²³⁷ Np	0.3%	²³⁰ Th	2%

^a Short-lived daughter of ¹³⁷Cs.
^b Short-lived daughter of ⁹⁰Sr.
^c Short-lived daughter of ²⁴³Am.
^d Short-lived daughter of ⁹³Zr.
^e Short-lived daughter of ²³⁷Np.
^f Decay products of ²²⁶Ra are in secular equilibrium; each decay product also represents 2 percent of inventory. The ²²⁶Ra decay products are generally short lived.

1.2 KEY TECHNICAL UNCERTAINTIES

As a result of analyses of regulatory issues and concerns related to demonstration of compliance with requirements in 10 CFR Part 60, the NRC and the Center for Nuclear Waste Regulatory Analyses (CNWRA) staff have identified KTUs that are relevant to colloid formation and transport (Nuclear Regulatory Commission, 1994). Natures and rates of geochemical processes that would either not affect or would favorably affect the ability of the geologic repository to isolate waste [10 CFR 60.122(b)(1)] and geochemical conditions that would either inhibit the formation of colloids or the transport of radionuclides by particulates and colloids [10 CFR 60.122(b)(3)(ii-iii)] are considered favorable conditions. The presence of geochemical processes that would reduce the sorption of radionuclides or adversely affect the performance of the EBS [10 CFR 60.122(c)(8)] is considered a potentially adverse condition. Also, the formation and transport of colloids may contribute to the controlled release requirements outlined for the EBS in 10 CFR 60.113(a)(1).

Table 1-3. Primary radionuclides contributing to repository inventory for vitrified wastes (adapted from Kerrisk, 1985)

Radionuclide and Percent of Total Activity for Various Decay Times							
10 ² yr		10 ³ yr		10 ⁴ yr		10 ⁵ yr	
⁹⁰ Sr	25%	²⁴¹ Am	31%	²³⁹ Pu	43%	⁹⁹ Tc	14%
⁹⁰ Y	24% ^a	²³⁹ Pu	28%	²⁴⁰ Pu	13%	⁹³ Zr	11%
¹³⁷ Cs	24%	²⁴⁰ Pu	16%	⁹⁹ Tc	11%	^{93m} Nb	11% ^c
^{137m} Ba	22% ^b	⁵⁹ Ni	6%	⁵⁹ Ni	11%	⁵⁹ Ni	8%
²³⁸ Pu	3%	⁹⁹ Tc	6%	⁹³ Zr	7% ^c	²³⁴ U	6%
⁶³ Ni	0.7%	⁹³ Zr	3%	^{93m} Nb	7%	²³⁹ Pu	6%
¹⁵¹ Sm	0.7%	^{93m} Nb	3% ^c	²³⁴ U	5%	²³⁰ Th	4% ^d
²⁴¹ Am	0.2%	²³⁴ U	2%	¹²⁶ Sn	0.8%	²²⁶ Ra	4%
²⁴¹ Pu	0.07%	²³⁸ Pu	1%	⁷⁹ Se	0.5%	¹³⁵ Cs	1%
²³⁹ Pu	0.05%	⁶³ Ni	0.6%	¹³⁵ Cs	0.5%	¹²⁶ Sn	1%
²⁴⁰ Pu	0.03%	¹²⁶ Sn	0.4%	²³⁰ Th	0.4%	⁷⁹ Se	0.4%

^a Short-lived daughter of ⁹⁰Sr.
^b Short-lived daughter of ¹³⁷Cs.
^c Short-lived daughter of ⁹³Zr.
^d Decay products of ²²⁶Ra are in secular equilibrium; each decay product also represents 4 percent of inventory. The ²²⁶Ra decay products are generally short lived.

One goal of the analyses is to identify areas of potentially high risk of noncompliance with the applicable regulatory requirement(s). As part of the development of Compliance Determination Strategies (CDSs) for the different regulatory requirements, a number of KTUs have been identified in the regulatory requirements related to colloids that will require detailed safety reviews of the pertinent portions of the DOE license application by the NRC. These strategies and the related KTUs have been published by the NRC as a part of the License Application Review Plan (LARP) (Nuclear Regulatory Commission, 1994). As specified in the license application content requirements of 10 CFR 60.21(c)(5) and Section 2.5 of the regulatory guide Format and Content for the License Application for the High-Level Waste Repository (FCRG), these KTUs must be addressed by the DOE in its license application.

1.2.1 Colloid-Related Key Technical Uncertainties

The KTUs related to colloids, selected from the regulatory requirements and published in the LARP, are described and discussed below.

1.2.1.1 Uncertainty in the Ability to Project the Nature and Rates of Quaternary Geochemical Processes

Colloid formation is affected by a number of geochemical processes. It is generally assumed that the processes occurring under natural conditions during the Quaternary period are also occurring at present and will continue to operate in the future. Unfortunately, the nature and rates of many of these processes are only poorly understood or lack the experimental data necessary for quantitative assessment. In addition, the impact of the repository, the HLW, and other human-introduced materials may have an effect on these processes that is not well constrained. Therefore, for the purposes of PA over the regulatory period of 10,000 yr, extrapolation is uncertain.

1.2.1.2 Uncertainty in Identifying Geochemical Conditions That Would Inhibit Particulate and Colloid Formation

Different processes could potentially contribute to the formation of particulates and colloids. Particulates and colloids can be produced by precipitation or condensation processes or by weathering or dispersion processes. These phases can be originally composed of radionuclides (termed radiocolloids) as, for example, particles from the spallation of wasteform or Pu(IV) colloid. These phases to which radionuclides sorb can be natural or man-made and produce what is often called a pseudocolloid. The construction of a repository in an undisturbed geologic system such as the unsaturated zone at Yucca Mountain could create significant amounts of particulate material. Many dissolved radionuclides are strongly attracted to solid surfaces. If the solid surfaces to which these radionuclides are attracted are particles moving with groundwater, these radionuclides would not be retarded by sorption processes. Given the uncertainty in identifying the geochemical conditions that could inhibit the formation of these phases, demonstration of compliance with 10 CFR 60.113(a)(1)(i)(B), 10 CFR 60.113(a)(1)(ii)(B), and 10 CFR 60.112 may be at risk.

Geochemical modeling efforts traditionally do not include consideration of particulates and colloids. Current geochemical computer codes (e.g., EQ3/6) cannot simulate the formation of particulates and colloids. Furthermore, the databases associated with geochemical codes do not contain information on particulates and colloids. As phases get smaller, the contribution of surface interactions to the overall energetics of the system studied becomes more important. Lacking thermodynamic and kinetic data on these phases, the geochemist is hard pressed to predict their effect on performance of the repository. Existing codes may need to be modified to take into account the effect of surface tension on the stability of small particles. Surface charge helps stabilize the small particles, keeping them dispersed through electrostatic repulsion. Furthermore, different size particles settle at different rates. (Also see Section 5.2.2.2, Table 5-1.) If coupled flow and transport modeling is attempted, consideration of particle size on diffusivity and rate of gravitational settling at various flow rates would be required. Also, experimental data on the surface tension of phases expected at the repository site would be needed.

1.2.1.3 Uncertainty in Characterizing the Chemistry of the Groundwater in the Partially Saturated Hydrologic Zone of Yucca Mountain, Nevada

Geochemical processes such as radionuclide precipitation, sorption, and complexation, as well as formation of colloids, are strongly influenced by groundwater chemistry (e.g., pH, ionic strength, and solute composition and concentration). For example, experimental data for various types of sorbents indicate that uranium sorption is strongly dependent on pH (Tripathi, 1984; Payne et al., 1992; Pabalan et al., 1993). The presence of complex-forming species reduces the amount of radionuclide sorbed on

mineral surfaces; this represents an unfavorable geochemical condition. The presence of colloids, which may enhance transport of radionuclides, is also a potentially unfavorable condition. Therefore, without knowledge of the groundwater chemistry in the partially saturated zone, including the presence and characteristics of colloids and particulates, it is not possible to determine if geochemical conditions present at the proposed repository are favorable or unfavorable to inhibition of radionuclide migration.

No known technique provides unambiguous and accurate measurements of the chemistry of pore waters in partially saturated media. The methods of extracting pore waters by high-pressure compression (Yang et al., 1988; Peters et al., 1992) and by ultracentrifugation (Edmunds et al., 1992; Puchelt and Burgfeldt, 1992) most likely impose some change in solution composition and are susceptible to contamination problems. *In situ* methods, such as low-vacuum electron microscopy and x-ray analysis, do not yet have the resolution to quantitatively measure solute concentrations in relatively dilute groundwater and remain to be tested for analyzing pore water chemistry in unsaturated media. Moreover, solution pH, which is a key parameter that controls radionuclide precipitation, sorption, and complexation, cannot be determined by *in situ* methods, and the pH of extracted pore water is likely different from that of *in situ* pore water. The chemistry of the groundwaters in the partially saturated zone of Yucca Mountain is therefore extremely uncertain.

1.2.1.4 Understanding the Effects of Degree of Saturation on Geochemical Processes such as Radionuclide Sorption, and Precipitation and Formation of Particulates and Colloids, and on the Transport of Radionuclides by Particulates, Colloids, and Complexes

The proposed repository is located in a hydrologically partially saturated horizon underneath Yucca Mountain. However, it is uncertain how the degree of hydrologic saturation will affect sorption, precipitation, colloid formation, and transport of radionuclides by particulates, colloids, and complexes. All batch sorption experiments and most column sorption studies are conducted under conditions in which the sorbing medium is fully saturated with water. It is not clear if unsaturated conditions will inhibit radionuclide migration more than fully saturated conditions, or whether unsaturated conditions can actually enhance migration of certain radionuclides. It is not known what the effect of degree of saturation is on the formation of particulates and colloids, and on the transport of radionuclides by particulates, colloids, and complexes. A recent study of the effect of hydrologically unsaturated conditions on colloid transport indicated that hydrophilic colloids are preferentially sorbed at the gas/water interface, while hydrophobic colloids sorb at both the gas/water and solid/water interfaces (Wan and Wilson, 1994).

Current approaches to modeling radionuclide retardation and transport in partially saturated media treat chemical interactions (e.g., sorption) in a way identical to that of fully saturated rock, except for modifying the effective porosity. However, it is uncertain if radionuclide sorption coefficients determined using fully saturated experiments can be extrapolated to conditions of variable saturation. Certain conditions may exist where partially saturated conditions enhance migration of radionuclides compared to fully saturated conditions. For example, at lower saturation, the amount of solid surface area in contact with the liquid phase may be reduced, thus diminishing sorption as a retardation mechanism for radionuclide transport. Therefore, it is uncertain if the geochemical conditions in the partially saturated zone of Yucca Mountain are favorable or unfavorable for inhibition of radionuclide transport.

1.2.1.5 Parametric Representation of Retardation Processes Involving Radionuclide-bearing Particulates, Colloids, and Complexes

PA calculations typically use a single retardation factor (R_f) to represent the attenuation of radionuclide transport. This factor is frequently based on an experimentally measured sorption coefficient (K_d), which is assumed to represent equilibrium sorption/desorption processes alone. However, other processes, including diffusion, dispersion, and precipitation, may contribute to retardation. Although using R_f simplifies transport calculations, it is empirical in nature and has no theoretical basis for extrapolation beyond the particular conditions of the initial experiments. It is well known that sorption of radionuclides on rock and mineral substrates is influenced by the physical and chemical characteristics of the groundwater (e.g., pH, composition, temperature) and of the substrate (e.g., mineralogy, surface area, surface properties). R_f (K_d) tends to be assigned as a property of the medium. This value does not accurately reflect the role of systematic chemical variations in determining the extent of retardation of radionuclide migration. The use of R_f also does not allow discrimination between the contributions of various processes involved in retardation. In addition, traditional transport codes that use a single R_f are based on systems that do not contain colloids.

1.2.1.6 Uncertainty in Identifying Processes Concerning Retardation of Radionuclides

As discussed in the following sections, there is a large degree of uncertainty in the types of retardation processes that operate in the geologic setting. Because colloid transport of radionuclides from the repository to the accessible environment is one transportation process that has been proposed, any information that can be used to quantify the contribution of colloids to transport will serve to resolve part of this uncertainty.

1.2.1.7 Uncertainty in Identifying Processes That May Adversely Affect the EBS

The formation of colloids may come through the degradation of the different components of the EBS (waste package, spent fuel, vitrified wastes). In addition, the formation and release of colloids from the wastefrom or from the waste package are directly related to the limited release requirements in 10 CFR 60.113(a)(1)(ii). The processes that operate on the EBS to form colloids are uncertain, and may compromise the ability of the EBS to isolate the waste.

1.2.1.8 Uncertainty in Identifying the Magnitude of the Effects of Geochemical Processes on Radionuclide Retardation

Because there is uncertainty in the processes that contribute to colloid formation and colloid-mediated transport of radionuclides in the geologic setting, there is necessarily uncertainty in the magnitude of these effects. It is also difficult to model the coupled effects of flow, transport, and colloid formation and transport. Experimental data that can be used to identify processes may also be useful in identifying important parameters for modeling the magnitude of the effects of these processes on radionuclide retardation.

1.2.1.9 Uncertainty in Identifying the Magnitude of Potentially Adverse Effects of Geochemical Processes on EBS Performance

The arguments used here are similar to those used in the preceding two KTUs. Uncertainty in identifying geochemical processes leads to uncertainty in estimating the magnitude of these processes.

This uncertainty is especially true given that unique materials and conditions far removed from those found in the unperturbed natural setting are anticipated in the EBS.

1.2.1.10 Prediction of the Releases of Nongaseous Radionuclides From Waste Packages During the Containment Period and From the EBS During the Post-Containment Period

This KTU considers that diffusion and convective transport will be the two significant mechanisms for the release of nongaseous radionuclides from penetrated waste packages and the EBS. The KTU discusses the uncertainty in estimating either diffusion or flow rates. Even if these factors can be estimated with any degree of certainty, additional uncertainty is present in the conceptual and/or mathematical models. Radionuclide concentrations in groundwater may be affected and possibly controlled to some extent by the formation of colloids. In addition, the formation of colloids will also affect the calculation of radionuclide transport from waste packages and the EBS to the near field and on to the accessible environment.

1.2.2 Nuclear Regulatory Commission Safety Review and Analysis

The NRC intends to conduct a detailed safety review and analysis of DOE data and analyses in support of the resolution of the KTUs described in Section 1.2.1, and additional KTUs that may develop prior to the issuance of the repository operational license. An example of an additional KTU would be the influence of man-made materials that may be introduced during the construction and operational phases of the repository on the generation, stability, and transport of colloids, and the resultant migration of radionuclides from the repository. (This subject is discussed further in Section 2.5.) Safety review plans and methodologies are currently being formulated.

2 GROUNDWATER COLLOIDS—NEVADA SITES AND OTHER FIELD STUDIES

2.1 COLLOID CLASSIFICATION RELEVANT TO HIGH-LEVEL WASTE

Colloids are differentiated from molecules and larger particles on a size basis [e.g., colloids refer to particles in the size range 10^{-8} to 10^{-15} m (see Figure 1-1)]. Colloid is not a classification based on chemical composition or on radionuclide content; however, the HLW management literature has adopted a terminology convention to differentiate between the possible various types of radionuclide-bearing colloids. This terminology, while not correct in the scientific sense, has nonetheless been retained in this report for the sake of consistency with the relevant literature and to facilitate the presentation of the material. This terminology is discussed in this section.

The colloids relevant to the subject of this report can be classified into three main categories: (i) groundwater colloids, (ii) real or true colloids, and (iii) pseudocolloids. Groundwater colloids are naturally occurring in all groundwaters, real colloids are produced by the aggregation of hydrolysed actinide ions, and pseudocolloids are generated by sorption of actinide ions, or colloids, on groundwater colloids. The three kinds of colloids are distinctively different from one another in their chemical properties. Some differences in their behavior as pertinent to sorption and transport in a geologic environment are described in this section.

2.1.1 Groundwater Colloids

Groundwater colloids are composed of inorganic and organic molecular constituents, a mixture of both, or microorganisms. They include weathered mineral products, hydrolysed precipitates of mixed metal ions, macromolecular components of dissolved organic carbon (DOC) (e.g., humic substances, loaded with metal ions), and biocolloids composed of microorganisms. Inorganic mineral colloids originate from two sources: solid phase precipitation from a supersaturated solution and particle release from the subsurface media (Apps et al., 1982). Colloidal particles may also be released by dissolution of rock matrix of which they are a part, or by changes in aqueous chemistry that act to re-suspend previously destabilized adsorbed particles. In addition, introduction of a low ionic strength water can redisperse submicron particles. Colloids of inorganic or organic nature, except biocolloids, are relatively small in size, namely <450 nm. As such, characterization of these colloids requires ultrafiltration techniques or ultracentrifugation (Kim, 1993). Groundwater colloids are chemically surface-active and therefore readily adsorb metal ions of higher charge ($Z \geq 2+$) through complexation or ion exchange processes (Kim, 1993).

2.1.2 Real or True Colloids

Hydrolysis is a primary step to polynucleation and thus generation of actinide colloids, which are known as real or true colloids. The relative tendency to generate real or true colloids of actinide ions can be expressed by hydrolysis order (Kim, 1993). The hydrolysis properties of actinide ions under aquatic conditions are mainly governed by the effective charge of a given ion. Other mechanisms of real colloid formation include polymerization, condensation, and precipitation processes. Real or true colloid formation is favored under alkaline conditions for dilute (low ionic strength) solutions. This formation is especially true in the case of highly charged, redox-sensitive species such as actinides (Maiti et al.,

1989; Choppin and Mathur, 1991). Tetravalent actinide ions are most unstable in aqueous solutions and readily undergo colloid generation even at pH=1. Olofsson et al. (1982a, b) indicated that the formation of colloids through this type of process is favored for the actinides in lower (+3, +4) valence states.

2.1.3 Pseudocolloids

In contrast to real or true colloids, pseudocolloids are formed when the radionuclides sorb on small particles already present in the groundwater. These particles may be either natural or introduced by human activity, and include organic and inorganic carbon, silica, clay particles, and oxyhydroxide compounds of metals such as Fe, Mn, and Al. The presence, stability, composition, and sorptive capacity of these particles are dependent on different aspects of the chemistry of the groundwater system, including pH, Eh, ionic strength, and $p(\text{CO}_2)$. Further complicating the behavior of pseudocolloids is the possibility of coating nonsorptive particles with sorptive materials (Robert and Terce, 1989).

The actinide ions with high electric charges ($Z \geq 2+$) are unstable in groundwater due to their strong hydrolysis reactions. Experiments with colloidal alumina of 20-nm average diameter have demonstrated that trace quantities of $^{228}\text{Th}(\text{IV})$, $^{241}\text{Am}(\text{III})$, and $^{237}\text{Np}(\text{V})$ are quantitatively sorbed on alumina in a wide pH range, where each ion becomes strongly hydrolysed. Such ions could also be easily adsorbed on other groundwater colloids. The migration behavior of actinide pseudocolloids can be understood only in conjunction with knowledge of the permeability of the colloids in a given aquifer system. Adsorption studies indicate that ^{137}Cs , ^{60}Co , and ^{152}Eu adsorb to colloids collected from the Nevada Test Site (NTS) groundwater (Kingston and Whitbeck, 1991). Comparisons of colloid and rock sorption coefficients suggest that Eu will preferentially adsorb to these colloids compared to tuffaceous rocks at the NTS. Adsorption to these colloids could lead to the formation of pseudocolloids. A potential consequence of this phenomenon is increased susceptibility of colloids to migration to the repository far field.

2.2 FIELD STUDIES OF GROUNDWATER COLLOIDS IN SOUTHERN NEVADA

A study involving 23 groundwater samples collected in central and southern Nevada was conducted by Kingston and Whitbeck (1991) to gain understanding of the concentration and size of colloids. The organic structures identified in the groundwaters include carbon-hydrogen (C-H) structures and carbonyl accompanied by amide I and II groups. The C-H groups may be due to pumping oil or fingerprint contamination, but the amide structures may indicate the presence of a humic or fulvic acid coating on a mineral colloid surface. Silica was present in all the samples as either cristobalite, fused silica, or amorphous silica (quartz was not present). Calcite appeared in some samples; however, it may have been an artifact of sampling and processing. Evidence of relatively small amounts of clay or zeolite was reportedly found in all samples.

The results from serial membrane filtration are summarized in Table 2-1. This table shows the colloid concentrations to be in the 0.27- to 1.35- $\text{mg} \cdot \text{L}^{-1}$ range, and the colloid size to be in the 1.0- to 0.03- μm range. The mean colloid concentration for the sites, excluding Peavine Canyon, Campground Spring, Whiterock Spring, and Topopah Spring due to missing data, was 0.9 $\text{mg} \cdot \text{L}^{-1}$. The mean concentration of groundwater colloids on the NTS was reported to be 0.58 $\text{mg} \cdot \text{L}^{-1}$ (Kingston and Whitbeck, 1991).

Table 2-1. Summary of colloid concentrations (adapted from Kingston and Whitbeck, 1991)

Size Range (μm)	Wells n=11		Springs n=9		Volcanic n=10		Carbonate n=7		NTS n=8		Off-Site n=12		All Sites n=20	
	\bar{x}	σ	\bar{x}	σ	\bar{x}	σ	\bar{x}	σ	\bar{x}	σ	\bar{x}	σ	\bar{x}	σ
> 1.0	0.27	0.20	0.58	1.25	0.61	1.16	0.11	0.08	0.64	1.32	0.25	0.18	0.41	0.34
1.0-0.4	0.21	0.13	0.21	0.16	0.26	0.14	0.13	0.06	0.15	0.08	0.29	0.17	0.21	0.14
0.4-0.1	0.54	1.21	0.20	0.13	0.22	0.11	0.15	0.10	0.14	0.08	0.55	1.14	0.39	0.90
0.1-0.03	0.40	0.49	0.24	0.08	0.28	0.14	0.22	0.08	0.23	0.05	0.39	0.47	0.33	0.37
1.0-0.03	1.15	1.79	0.64	0.32	0.76	0.33	0.51	0.19	0.53	0.18	1.19	1.70	0.90	1.35

\bar{x} \equiv mean colloid concentration in $\text{mg} \cdot \text{L}^{-1}$
 σ \equiv standard deviation
n \equiv number of samples
Peavine Canyon, Campground Spring, Whiterock Spring, and Topopah Spring are omitted due to missing data.

Since the carbonates in different locations are expected to weather differently, and despite changes in water chemistry, lithology, and treatments such as well construction and increased seismic activity, a very surprising and significant conclusion of the study was that no connection between colloid concentration and sample environment was detected (with the exception of a few outliers). This statement is based on the following three sets of geologic conditions: (i) carbonate versus volcanic sources: despite differences in lithologies and chemistry including concentration of Ca, Mg, K, HCO_3 , SiO_2 , and total dissolved solids (TDS) concentrations (see Table 2-2); (ii) well versus spring: although well samples were from disturbed environments and spring samples were from natural environments; and (iii) on and off the NTS location. The outliers and their concentrations were as follows: Topopah Spring ($> 25 \text{ mg} \cdot \text{L}^{-1}$), Whiterock Spring ($> 16 \text{ mg} \cdot \text{L}^{-1}$), and Beatty Well 2 ($> 6 \text{ mg} \cdot \text{L}^{-1}$). The water chemistries of Topopah Spring and Whiterock Spring are quite similar to the other sites. Beatty Well 2 is unique in that it has the highest TDS of all the sites ($772 \text{ mg} \cdot \text{L}^{-1}$).

2.3 GROUNDWATER RADIOCOLLOIDS IN OTHER FIELD STUDIES

Field studies indicate that the tendency of radionuclides to be associated with a certain size fraction is dependent upon the radionuclide under consideration. The quantitative information provided in this section covers field sites of interest to HLW disposal from around the world. For groundwaters, marsh water, and river water in Norway, Salbu et al. (1987) reported that more than 80 percent of the radionuclides ^{58}Co , ^{60}Co , ^{54}Mn , ^{65}Zn were associated with colloids, pseudocolloids, and particles larger than 450 nm. In the Koongarra uranium deposit in the Alligator Rivers Uranium District, Australia, Short et al. (1988) observed that $^{230,232}\text{Th}$ sorbed strongly to colloids in the 18- to 1,000-nm range, while only minor portions of $^{234,238}\text{U}$ are associated with particulate matter. Also at Koongarra, Seo (1990) observed a minor uranium colloid in one water sample, and estimated that only 0.1 to 0.5 percent of the total uranium was associated with the colloidal phase. In a field study at Los Alamos National Laboratory

Table 2-2. Summary of chemical data (adapted from Kingston and Whitbeck, 1991)

	Wells n=11		Springs n=9		Volcanic n=10		Carbonate n=7		Alluvium n=3		NTS n=8		Off-NTS n=12		All Sites n=20	
	\bar{x}	σ	\bar{x}	σ	\bar{x}	σ	\bar{x}	σ	\bar{x}	σ	\bar{x}	σ	\bar{x}	σ	\bar{x}	σ
Ca ²⁺	27.4	25.5	39.5	25.8	23.7	25.2	45.9	24.4	22.0	7.9	36.2	34.4	31.9	18.0	72.0	203.5
Mg ²⁺	7.4	9.9	13.3	9.5	7.8	10.8	21.4	4.5	4.0	3.0	11.0	12.2	10.0	8.3	10.5	10.0
Na ⁺	81.0	62.4	24.0	22.5	40.6	35.9	40.0	45.5	123.9	92.5	55.1	44.6	48.3	61.2	51.3	53.6
K ⁺	5.3	4.2	4.6	3.1	3.4	2.4	6.6	4.6	7.7	3.1	5.7	4.2	4.4	3.2	4.9	3.6
Cl ⁻	18.7	20.9	11.6	7.4	10.7	4.8	14.8	11.5	34.0	37.8	12.8	8.8	16.7	19.3	15.0	15.5
SO ₄ ²⁻	50.1	48.6	39.0	51.7	32.3	45.7	44.8	34.2	95.3	77.1	44.9	51.9	43.9	49.5	44.3	49.4
HCO ₃ ⁻	243.6	164.0	196.1	80.5	150.6	84.1	334.5	118.8	245.0	117.2	235.6	167.0	206.0	89.9	218.8	126.7
SiO ₂	46.9	15.6	35.3	20.2	46.2	14.4	22.4	9.5	60.7	18.6	46.2	19.8	36.7	17.3	40.8	18.6
TDS	358.6	199.5	274.8	120.4	229.4	77.8	403.1	178.4	470.0	263.3	319.6	158.5	301.2	181.3	314.9	165.9
pH*	7.76	0.59	7.41 ^a	0.53	7.48	0.60	7.66 ^a	0.63	7.89	0.20	7.54	0.53	7.62 ^a	0.63	7.56	0.57
Temp	27.3	7.0	20.9	7.5	22.2	8.2	26.5	8.6	25.3	2.0	26.6	7.45	17.3	9.6	23.9	7.8

\bar{x} = mean value; σ = standard deviation; n = number of samples
 Concentrations reported in mg · L⁻¹
 Temperature reported in °C
 * = Field pH when available; otherwise, lab pH
 a = pH of 7.07 obtained from field used for Crystal Pool
 Peavine Canyon, Campground Spring, Whiterock Spring, and Topopah Spring are omitted due to missing data.

(LANL), Penrose et al. (1990) observed that 85 percent of ^{242}Pu tended to be associated with particles greater than 25 nm, while 43 percent of ^{243}Am was associated with particles less than 2 nm in diameter. These actinides had migrated up to 3,000 m from the inferred point of origin, but there is some question as to whether this migration represented actual subsurface transport or surface runoff. In an oligotrophic lake in Wales, Orlandini et al. (1990) observed that over 80 percent of the actinides Am, Th, and Pu were associated with organic compounds greater than 450 nm in size.

At the candidate repository site at Gorleben, Germany, Kim et al. (1987b) noted that groundwater concentration of trace elements with greater than 2+ oxidation state increased in direct proportion with increasing DOC concentration. However, a poor correlation existed between DOC and radionuclide concentration for mono- and divalent species. They attributed this poor correlation to complexation with humic acids and also fulvic acids to a lesser extent. Orlandini et al. (1990) observed that the more reduced species Am^{3+} , Th^{3+} , and Pu^{4+} complexed strongly with colloidal organic material. Maest et al. (1985) observed that chelation of radionuclides decreased with the degradation of the organic compound ethylenediaminetetraacetic acid (EDTA). Because the complexation of metals by organic compounds is dependent on the number of sites available through proton dissociation, the degree of complexation will vary as a function of solution pH in a manner analogous to metal oxides. Binding of metals reduces the electrostatic repulsion in the anionic groups in the humic molecules. This reduction in electrostatic repulsion results in a more compact, hydrophobic molecule that can coagulate into larger aggregates that form colloids (Choppin, 1988). In an Oak Ridge National Laboratory analysis of contaminated sediments, Means et al. (1978a, b) noted that ^{60}Co and the actinides ^{241}Am , ^{238}Pu , and ^{244}Cm were associated with particles from 200 nm to 2 μm in diameter, probably due to organic and Mn-oxide coatings on clay particles. In addition, essentially all the ^{60}Co and more than 70 percent of the uranium in the laboratory experiments are associated with organics above a molecular weight of 700. In tests on a shallow sandy aquifer, Gaffney et al. (1991) observed that all actinides, from both natural sources and fallout, were migrating with organic particulate matter (<450 nm). In the Cigar Lake uranium deposit in Saskatchewan, Canada, Vilks et al. (1988) observed higher association of uranium within the orebody as compared with the nonmineralized sandstone. The authors propose that the clay zone surrounding the orebody acted as an efficient filter to remove uranium-bearing colloids from suspension.

The observations reported in this section indicate that factors influencing the size and distribution of a particular radionuclide could be quite complex, and depend on a large number of variables; therefore, detailed field data may be required in order to include colloid release and transport in the PA calculation for Yucca Mountain repository site. Although a comprehensive study has been reported on the characterization of groundwater colloids around the Yucca Mountain site (Kingston and Whitbeck, 1991), very little data are available on radiocolloids. There appears to be a need for additional field data using well-planned large-scale field experiments. Perhaps additional data from the NTS could provide some relevant and useful information.

2.4 COLLOIDAL ORGANIC MATTER

Naturally occurring organic matter in soils and groundwaters consists of living organisms (e.g., bacteria and plants) and organic molecules in dissolved or particulate form. Dissolved organic matter is that material that passes through a 0.45- μm filter (Thurman, 1985a; Choppin, 1988) and represents the bulk of the organic matter in natural systems. Dissolved organic matter consists of a variety of forms (Figure 2-1). Fatty and amino acids, carbohydrates, and other simple hydrocarbons are smaller than the

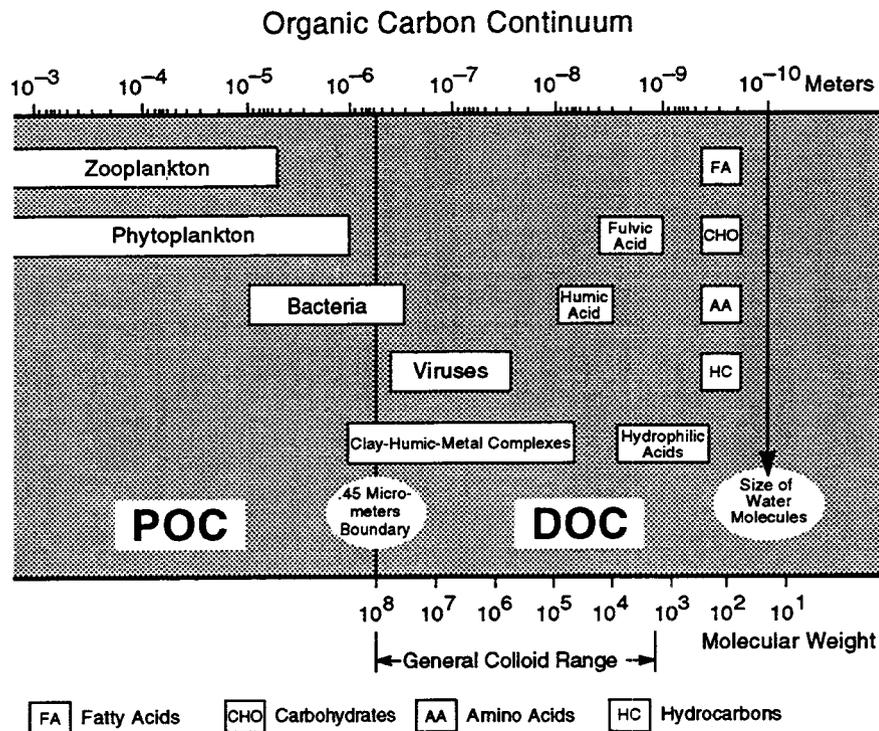
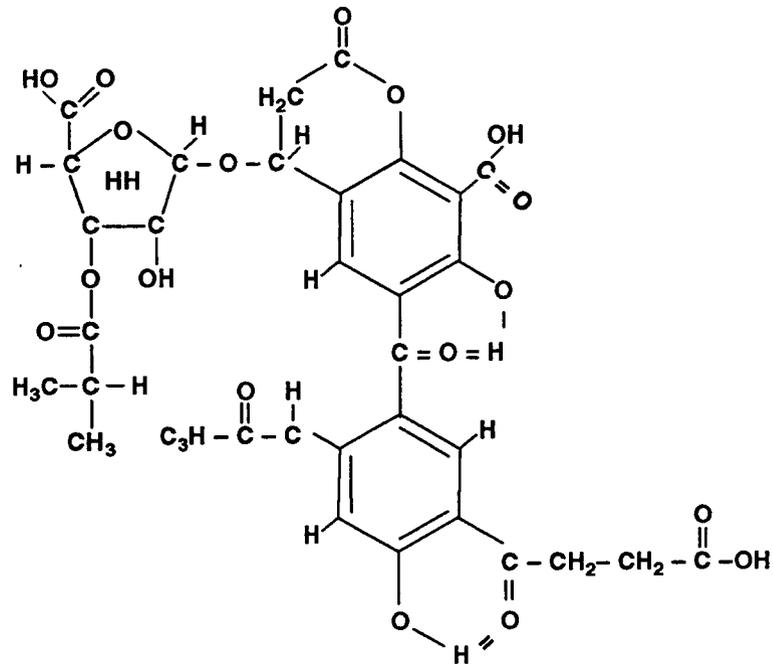


Figure 2-1. Continuum of particulate and dissolved organic carbon in natural waters (adapted from Thurman, 1985a)

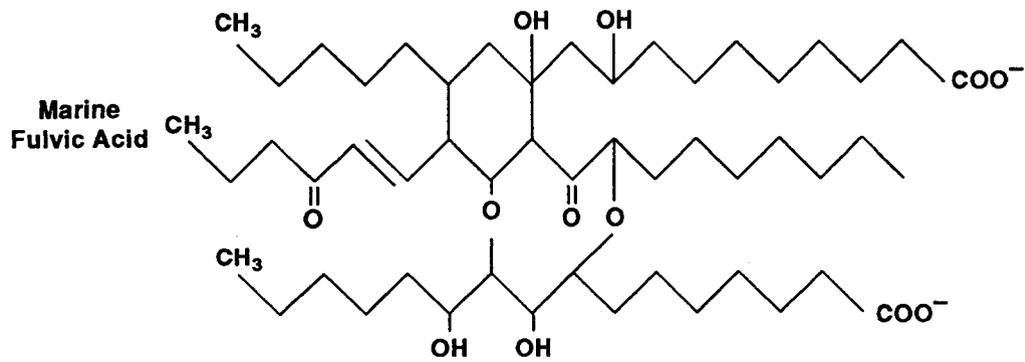
defined size for colloidal materials and are considered to be in solution. The colloidal forms may consist of large polymers, complexes, and particulates. The colloidal forms of dissolved organic matter generally constitute less than 10 percent of DOC (Thurman, 1985a).

Bacteria have a significant impact on the forms of organic matter found in groundwater. They are essential to the decomposition of macromolecules such as cellulose. Bacteria also reproduce, and they secrete organic compounds that help in the attachment to substrates or in complexing dissolved material for uptake by the organism (Hersman et al., 1993). Microorganisms also affect the overall chemistry of the subsurface environment. They are essential to the weathering process and affect the chemistry of groundwaters through aerobic or anaerobic metabolic processes (Chappelle, 1993).

Humic substances are divided into three structurally different groups based on solubility. Fulvic acids are soluble at all pH values, while humic acids are soluble only at pH greater than about 3.5. Humins are insoluble under all pH conditions, due to the strength of bonds formed with inorganic ions (Kim et al., 1987b; Choppin, 1988). Intermediate between humic acid and humins are soluble humic colloids. The humic substances (humic and fulvic acids) are macromolecules 2 to 50 nm in diameter, with molecular weights up to 100,000 amu (Thurman, 1985a). Some humic acids may have diameters as large as 110 nm, with molecular weights of 2,000 amu (Österberg et al., 1993). The humic substances are characterized by a combination of aromatic and aliphatic components (Figure 2-2). Chemical composition and structural determination of the humic substances have been the subjects of many investigations (Thurman, 1985a; Carlsen, 1989; Higgs et al., 1992). The reactive parts of these macromolecules consist



(a)



(b)

Figure 2-2. Example structures of (a) humic acid and (b) fulvic acid (adapted from Morel and Hering, 1993)

of various functional groups: (i) carboxylic acids (COOH), (ii) phenols (OH), (iii) ketones (C=O), and (iv) amines (NH₂). The functional groups are important in the sorption of dissolved or colloidal forms of radionuclides (Carlsen, 1989).

Humic substances in groundwater tend to be more aliphatic in character than those found in soils (Carlsen, 1989). Thurman proposed that the difference is due to percolating rain waters leaching the more soluble fulvic acid fraction from the soil (Thurman, 1985a).

The humic and fulvic acids are probably the most important ligands originating from the partial decomposition of plant materials (Tipping and Higgs, 1992). Approximately 50 percent of the DOC in groundwaters consists of fulvic and humic acids (Thurman, 1985a). Groundwater concentrations of DOC range from 0.05 to 0.25 mg · L⁻¹, of which 0.03 to 0.10 mg · L⁻¹ is humic material (Thurman, 1985a).

2.5 COLLOIDS FROM OTHER THAN GROUNDWATER AND HIGH-LEVEL WASTE

Human activity associated with a HLW repository may also introduce colloidal materials in the form of organic matter used in drilling, processing the waste, and constructing the repository (Means et al., 1978a, b; Means and Wijayarathne, 1982). Although a detailed discussion of this subject, including the types of colloids that might be generated and the identification of ones that may lead to formation of transportable pseudocolloids, is not possible at this time, a recent study related to the Yucca Mountain site reports that 560,000 m³ of shotcrete is expected to be emplaced in repository drifts alone (Meike, 1993). For only one of the exploratory shaft portal facilities, the quantity of man-made material that will be introduced during a year is estimated to be 26,000,000 gal. of water, 250,000 gal. of diesel fuel, 10,000 lb of rockbolt resin, 1,800 sq ft of extruded polystyrene, 50 cu yd of bentonite clay, and 250 gal. of cable lubricant (Meike, 1993). Since the construction and operational period of a HLW repository are expected to be on the order of 50+ yr, the quantities of expected human-introduced materials are quite high. Therefore, the influence of human-introduced materials on the generation and transport of radionuclides would have to be addressed in the license application.

In addition to the foreign materials that may be introduced in the repository during construction, a significant source of colloid will be the degradation products of the metallic components of the waste package. Elements such as Fe and Al and their alloys, if used in the waste package, have the potential of releasing substantial amounts of colloids in the groundwater prior to the contact of the intruding waters with spent fuel and vitrified wasteform. Colloids formed as a result of waste package material degradation could act as nuclei for the generation of pseudocolloids upon release of radionuclides from spent fuel and vitrified wasteform. Fe ions from the waste package can lead to an increase in the radioactivity in colloidal phase by a factor of five, as shown in Figure 2-3 (McVay and Buckwalter, 1983). In this figure, leaching data on vitrified wasteforms were obtained through tests in groundwaters with and without Fe present.

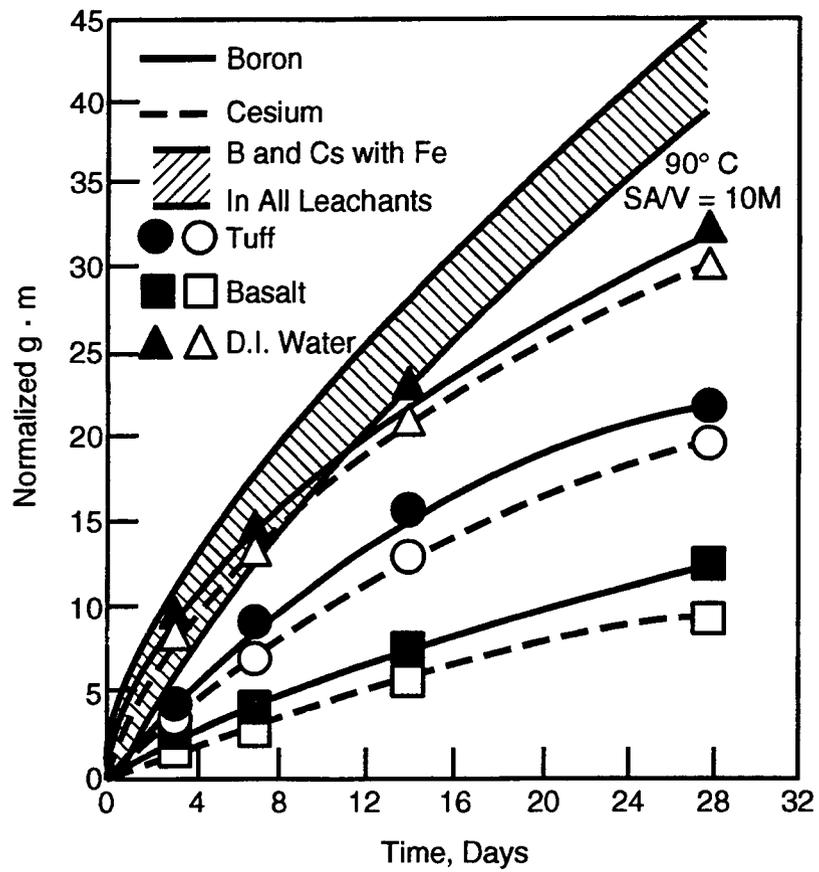


Figure 2-3. Effect of Fe in the leachant on corrosion of PNL-76-68 borosilicate glass (adapted from McVay and Buckwalter, 1983)

3 POTENTIAL SOURCES OF COLLOIDS IN A GEOLOGIC HIGH-LEVEL WASTE REPOSITORY

In this section, the principal sources of colloids in a geologic repository are discussed. The mechanisms and controls on the rates of colloid generation and growth are described. This section also provides a discussion of the subject of radiocolloid releases from spent fuel and vitrified wastefoms in the context of their relevance to the Yucca Mountain repository site, presenting experimental data and discussing the relevant uncertainties.

3.1 COLLOIDS AND THE REPOSITORY ENVIRONMENT

The three principal sources of colloids and radiocolloids in a geologic repository environment are: (i) naturally occurring groundwater colloids; (ii) EBS corrosion products and man-made materials introduced during construction and operation of the repository; and (iii) HLW, both spent fuel and vitrified wastefoms.

Naturally occurring groundwater colloids such as clays and organics may provide a surface onto which soluble radionuclides can adsorb or precipitate, thereby generating pseudocolloids of radioactive elements that may affect the rate of radionuclide transport from the repository to the accessible environment. Colloid transport is discussed in more detail in Section 5.

During the initial wetting period when the thermal and radiation output of the waste is highest, the waste package material could introduce substantial amounts of corrosion products (due to enhanced corrosion), which may increase the concentration of colloids in the groundwater. Waste package corrosion products could also introduce colloids of different chemical composition than initially present in the repository. Since the materials and the design of the waste package have not yet been defined, the composition of the corrosion products is speculative. However, most corrosion products released to the groundwater could be expected to be in the form of relatively insoluble oxyhydroxides that could provide a large surface area for the sorption of soluble radionuclides.

The current conceptual design for the proposed HLW repository at Yucca Mountain does not rely on backfill material to separate the waste package from the surrounding geologic medium. However, should this design be modified in the future to include backfill as a means of enhancing the containment capabilities of the EBS, the backfill is not expected to remain intact indefinitely. Therefore, a repository PA should take into account the effects of the degradation of backfill on the generation, sorption, and transport of radionuclides in colloidal form. In addition to backfill material, a potentially significant source of colloids would be man-made organic and inorganic materials introduced during the construction and operational phase of the repository.

Near the waste package, the temperature is expected to be high due to the thermal output of the HLW. As a consequence, many radionuclides are expected to have high solubility limits within the waters near the EBS. However, as the soluble radionuclides are transported from the EBS, the temperature of the aqueous solution would decrease until it reaches ambient values. Under such a scenario, hydrolysis, nucleation, and complexation with ligands could lead to the formation of colloids. Also, as radionuclides are transported from the EBS, the concentration of their soluble species is expected to decrease (due to hydrodynamic dispersion) to levels sufficiently low that supersaturation is no longer required for nucleation. Consideration of this aspect of radionuclide migration in a geologic environment when

evaluating the performance of a HLW repository may require detailed information, such as waste package design, engineered barrier design, waste package and repository heat loading profiles, geochemistry of the groundwaters, and solubilities of various radionuclides as a function of temperature, pH, and water chemistry.

3.2 MECHANISMS OF COLLOID FORMATION

Alteration of spent fuel or vitrified wasteforms may occur as air and water contact the wasteform after breach of the waste package. The processes of oxidation, leaching, and physical breakup of the wasteforms may produce a variety of colloidal particles. Real or true colloids can be formed through condensation or dispersion (Apps et al., 1982). Condensation denotes the formation of nuclei or colloids when the groundwater becomes supersaturated with respect to a given species. The species' molecules flocculate to form clusters that can become a suspension of radioactive particles or colloids. Apps et al. (1982) cited studies in which the formation of colloidal particles of the 3+, 4+, and 6+ actinides as well as Pd, Sn, and Pb has been observed. Tetravalent actinides have a high tendency to hydrolyze, leading to the formation of polymeric complexes that eventually precipitate as insoluble particles (Jensen, 1982). Wildung et al. (1979) suggested that when Pu^{4+} is a product of the reduction of higher oxidation states, it can extensively hydrolyze and produce insoluble species. In contrast to nucleation, dispersion processes can create colloids through the mechanical or chemical breakup of larger particles into smaller ones.

The mechanism of colloid formation by condensation can be described as comprising two steps: (i) nucleation and (ii) growth. These two steps are briefly discussed below.

3.2.1 Nucleation

Two types of nucleation may take place: (i) homogeneous nucleation, which occurs in solution in the absence of a substrate; and (ii) heterogeneous nucleation, which occurs on a substrate.

3.2.1.1 Homogeneous Nucleation

Homogeneous nucleation is typically the result of high supersaturation of the solution with respect to a given dissolved species. The nuclei form in the bulk solution and are not attached to a substrate. For the occurrence of homogeneous nucleation, a critical level of supersaturation must be reached; this critical supersaturation can exceed the equilibrium concentration by several orders of magnitude. After critical supersaturation has been reached or exceeded, the nucleation rate becomes a strong function of the concentration, and the rate can increase by several orders of magnitude with small increases in the supersaturation. The rate at which colloids can form due to homogeneous nucleation can be described by the following expression [Eq. (3-1)], originally suggested by Volmer and Weber (1926) and more recently discussed by Randolph and Larson (1971):

$$R_{\text{HN}} = C_p e^{-\frac{\Delta G^*}{kT}} \quad (3-1)$$

where

$$R_{\text{HN}} = \text{rate of homogeneous nucleation}$$

ΔG^*	=	free energy of nucleus formation
k	=	Boltzmann's constant
C_p	=	proportionality constant (empirical)
T	=	absolute temperature

However, because homogeneous nucleation is not the only means by which nucleation occurs in natural systems (i.e., independent of heterogeneous nucleation), the use of this expression for predicting homogeneous nucleation alone may not be sufficient.

3.2.1.2 Heterogeneous Nucleation

Heterogeneous nucleation occurs when nuclei form on existing surfaces, typically of a different chemical composition. As such, heterogeneous nucleation can be one of the mechanisms responsible for the formation of pseudocolloids. Heterogeneous nucleation can take place at relatively modest supersaturations. Nielson (1964) noted that Eq. (3-1), for the rate of homogeneous nucleation, at a fixed temperature, can be approximated with a power-law function of supersaturation [Eq. (3-2)]. Nielson's approximation is based on two assumptions: (i) nucleation does not take place at low supersaturations, and (ii) homogeneous and heterogeneous nucleation occur simultaneously.

$$R_N = k(C - C_m)^i \quad (3-2)$$

where

C	=	solute concentration
C_m	=	concentration greater than the saturation concentration below which nucleation does not occur
i, k	=	adjustable parameters (empirical)

This expression is more commonly known as the Miers nucleation model and has been shown to provide a good representation of experimental nucleation data (Bonano et al., 1984). The parameter k is typically assumed to be a function of temperature, whereas the exponent i is not; the value of i seldom exceeds 21 and even can be slightly negative (Bonano et al., 1984).

3.2.2 Growth

Once formed, radiocolloids may change in size. Colloids that form by nucleation can grow in a way similar to the growth of crystals in saturated solutions. Such growth consists of two primary steps: (i) diffusion of dissolved species to the surface of the existing colloids, followed by (ii) surface-reaction-like mechanisms in which the solute is oriented into the crystal lattice. In systems that are not mechanically agitated, the colloid growth rate typically is diffusion-limited (i.e., the rate at which the dissolved species diffuse through the concentration boundary layer surrounding the colloids is much slower than the surface-reaction rate). Randolph and Larson (1971), assuming a linear dependence of the reaction rate on supersaturation, proposed that the growth rate of a colloid can be expressed as:

$$\frac{dm}{dt} = \frac{DA_c}{\delta + \frac{D}{k_r}} (C - C_s) \quad (3-3)$$

where

- m = mass of the colloid
- A_c = surface area of the colloid
- $C - C_s$ = degree of saturation in solution
- D = diffusion coefficient
- k_r = surface-reaction rate constant
- δ = thickness of the concentration boundary layer

For colloids of identical shape, regardless of their size, Eq. (3-3) can be reduced to:

$$\frac{da}{dt} = G = k_G s \quad (3-4)$$

where

- a = equivalent radius of the colloid
- t = time
- G = growth rate
- s = saturation ($C - C_s$)
- k_G = $DK/[3K_v\rho_c(\delta + D/K_v)]$
- K, K_v = size-dependent shape factors for the colloid
- ρ_c = density of the colloid

Equation (3-4) assumes that the growth is independent of size; however, experimental data suggest differently. Therefore, frequently, a size-dependent growth rate is used (Randolph and Larson, 1971) in Eq. (3-4), such as:

$$G = G_0(1 + ma)^n \quad (3-5)$$

where

- G_0 = growth rate for $a = 0$
- m, n = adjustable parameters (empirical)

3.2.2.1 Influence of Temperature on Nucleation and Growth

The Arrhenius-type expression [Eq. (3-1)] demonstrates that nucleation is a function of temperature. Just as the degree of saturation (and therefore supersaturation) varies as a function of temperature, so too does the growth rate. For this reason, PA models should incorporate consideration of repository temperature as a function of time and space in order to estimate the rates of colloid generation and growth in the repository. This type of temperature information, which is a function of the repository design and properties of the geologic formation, is relatively easy to obtain or generate. Uncertainties associated with including nucleation and growth mechanisms in PA may include concentration and supersaturation levels of various species throughout the repository, the lack of data concerning nucleation and growth rates, and the extent in time to which colloid generation may continue once initiated.

3.3 SPENT FUEL AND VITRIFIED (GLASS) WASTEFORMS

Many technical concerns raised in the KTUs described in Section 1.2.1.1 pertain to colloid formation associated with wasteform degradation, the need to simulate colloid formation in laboratory experiments, and colloid stability. In the next two sections, pertinent literature is reviewed and existing information is discussed to substantiate the KTUs.

3.3.1 Spent Fuel

During spent fuel dissolution, the surface of the spent fuel alters by oxidation and the precipitation of secondary phases containing low-solubility elements such as uranium and other actinides released by the dissolution process. Formation of an altered layer on the spent fuel surface may help inhibit further alteration. However, the altered layer may be mechanically or chemically disrupted or have micro-porosity, allowing continued access to the spent fuel. For this reason, the altered surface layer formed is unlikely to protect completely against further dissolution of the spent fuel matrix. Because the altered layer may be unprotective, the spent fuel may continue to dissolve and alter, and serve as a potential source for colloid formation.

The relative magnitudes of the rates of spent fuel dissolution and formation of the surface alteration layer are a function of material properties such as electrical charge, crystallographic orientation, and aqueous phase flow rate. As long as the total mass transfer from dissolving phases is greater than the growth of the secondary phases, the aqueous phase may become supersaturated with respect to the secondary phases. This supersaturation would be applicable in near-static liquid. Under this condition, leachate will maintain supersaturation and growth of secondary phases (e.g., altered layers and colloids). Under low-aqueous flow conditions, dissolution of low-solubility phases is likely to be interface controlled (Mendel, 1984).

3.3.1.1 Radionuclide Releases from Spent Fuel

Wilson (1990a, b; 1991) reported that Pu, Am, Cm, and Si colloids form during the dissolution of spent fuel in immersion tests with J-13 well water at 25 and 85 °C. Figure 3-1 illustrates the release of $(^{239+240}\text{Pu})$, ^{241}Am , and ^{244}Cm in immersion tests at 85 °C. The first cycle shown in the figure used as-received spent fuel (bare matrices). After removing secondary phases formed on the surface, the second cycle retested the first-cycle samples that had been placed into new leachant, and the third cycle

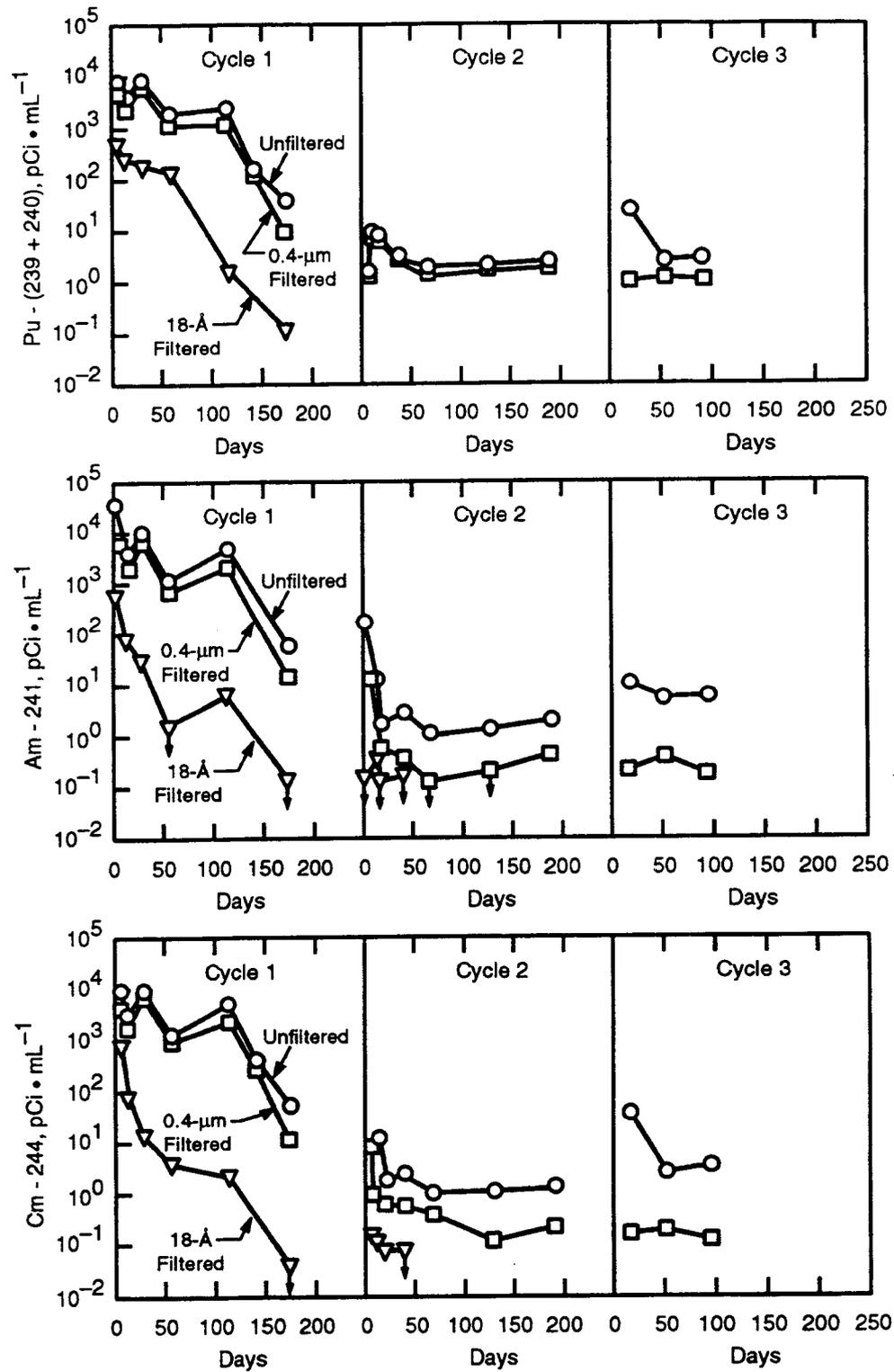


Figure 3-1. Effects of filtration on radioactivities released from bare spent fuel at 85 °C in J-13 groundwater (adapted from Wilson, 1990b)

was a repetition using second-cycle samples. Sampling during the test cycles was done by extracting small aliquots of fluid from the reaction vessel and replacing it with the same amount of fresh J-13 well water. Leachates were filtered through 0.4- μm and 1.8-nm filters. The difference in the levels of radioactivity between the filtered and unfiltered leachates was attributed to colloids of a size greater than 1.8 nm (Wilson, 1990b). Uranium colloids have also been identified in unirradiated UO_2 dissolution experiments conducted in J-13 well water at room temperature as shown in Figure 3-2 (Veleckis and Ho, 1991), and in UO_2 and spent fuel dissolution in brine and deionized water in the temperature range of 25 to 150 $^{\circ}\text{C}$ (Wilson, 1985; Gray and McVay, 1984; Wang, 1981). In Figure 3-2, the difference in uranium concentration between filtered and unfiltered leachates (> 1.8 nm) was attributed to colloids.

3.3.1.2 Mechanisms for Colloid Formation

Colloids may form during the dissolution of spent fuel by: (i) nucleation process—precipitation of colloidal-size secondary phases from solution, (ii) dispersion process—detachment of fuel grains and spallation of altered layers, and (iii) sorption of dissolved nuclides onto pre-existing colloidal material. The following discussion outlines these mechanisms and presents supporting experimental evidence.

Nucleation Processes

Despite the difficulties in distinguishing among colloids formed by the different mechanisms, evidence suggests that nucleation and condensation to form colloids from spent fuel may occur under conditions anticipated in a geologic repository (Wilson, 1990a, b, 1991; Gray and McVay, 1984; Veleckis and Ho, 1991; Wang, 1981). To evaluate the long-term contribution of these mechanisms of colloid formation to repository performance, it is important to understand the rate of colloid nucleation.

Radiocolloid nucleation may be initiated by: (i) hydrolysis, (ii) complexation with ligands such as carbonates or organic molecules, and (iii) oxidation/reduction in response to alpha decay (Newton et al., 1986). The hydrolysis of actinides is well documented (Kim, 1986). Through subsequent dehydration of the hydrolyzed ions (Figure 3-3), the condensation of ions leads to the formation of colloids (Maiti et al., 1989; Stumm and Morgan, 1981; Wendt, 1973). Similarly, large clusters of ions or ligand complexes may lead to the formation of colloids. Growth of colloids may also occur by accumulation or flocculation. Conversely, growth may be inhibited by disintegration. As discussed in Section 3.2.1.1, homogeneous nucleation theory has been developed to address nucleation in the absence of a substrate. Although heterogeneous nucleation on a substrate is also likely in the repository, the uncertainty regarding the geometries involved makes calculation much less straightforward, and empirical methods are commonly used. However, heterogeneous nucleation can be interpreted based on homogeneous nucleation in a relatively simple way. The following discussion is based on the evaluation of homogeneous nucleation of single elements or oxides.

The homogeneous nucleation rate of colloids can be expressed as (Ahn et al., 1993; Richardson and McSween, 1989)

$$R_{\text{nuc}} \approx C_s k \frac{T}{h} e^{-\Delta G_d/RT} e^{-\Delta G_c/kT} \quad (3-6)$$

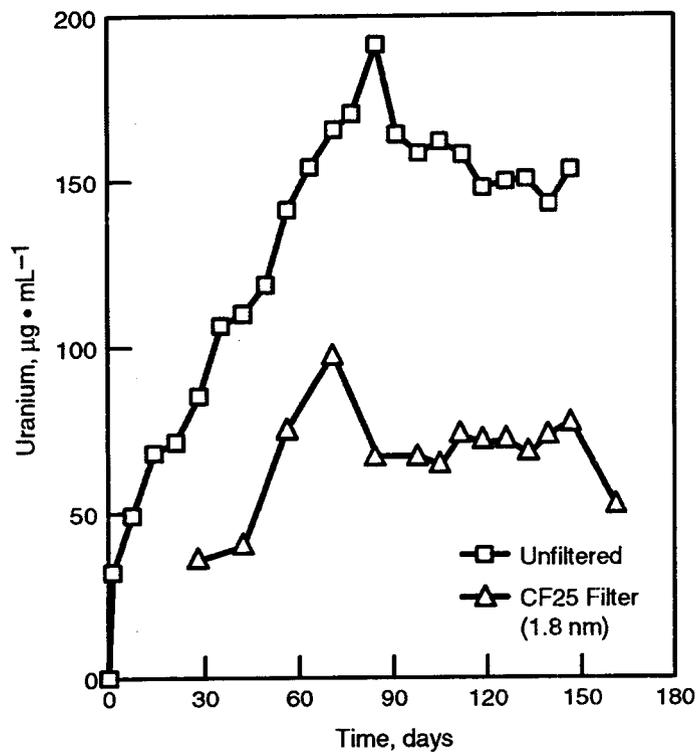
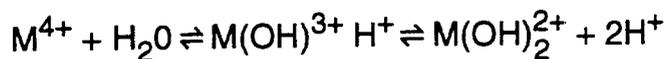


Figure 3-2. Filtering effects on the uranium concentrations in the dissolution of polycrystalline UO_2 in J-13 groundwater at room temperature (adapted from Veleckis and Ho, 1991)

Hydrolysis



Condensation

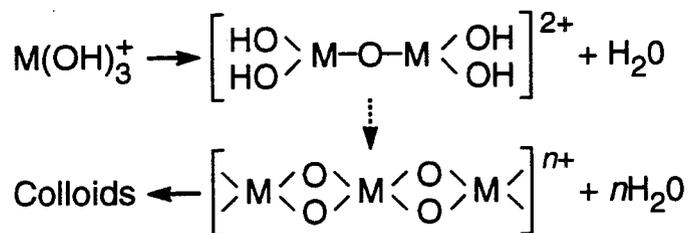


Figure 3-3. Hydrolysis and condensation processes for colloid formation (adapted from Maiti et al., 1989)

where

- C_s = concentration of species of interest
- k = Boltzmann's constant
- T = temperature
- h = Planck's constant
- ΔG_d = activation energy for the ionic diffusion in leachates
- R = gas constant
- ΔG_c = activation energy for the formation of the critical nucleus

For a spherical particle

$$\Delta G_c = \left[\frac{(16 \pi \gamma^3 M^2)}{(3 \rho^2 \Delta G_v^2)} \right] \quad (3-7)$$

where

- γ = surface energy per unit area of the colloid
- M = molecular weight of the secondary phase
- ρ = density of the secondary phase
- ΔG_v = free energy change per unit volume

and ΔG_v may be approximated by (Stumm and Morgan, 1981; Sauthoff, 1976)

$$\Delta G_v = -R T \ln \left[\frac{C_s}{C_o} \right] \quad (3-8)$$

where

- C_o = solubility limit for the species

Alternatively, ΔG_v may be estimated by $-R T \ln[Q/K]$, where Q is the ion activity product to the power of the stoichiometry of the ion, and K is the equilibrium value of Q .

Equations (3-6), (3-7), and (3-8) include a number of unknown parameters that are difficult to measure. Using available experimental data, it is possible to estimate R_{nuc} , ΔG_v , and γ . In experimental systems, the rate of colloid nucleation (R_{nuc}) may be estimated for actinides such as uranium and Pu by the product of (number of particles per unit leachate volume) \times (replenished leachate volume)/(replenishment time). This estimate is based on the assumption that leachate concentrations are

constant despite nearly 100 percent replenishment of the leachates. Alternatively, R_{nuc} may be estimated by the decrease in leachate concentration after a transient period of leaching.

In leaching experiments on a number of spent fuel samples in J-13 well water at 25 °C, about 200 pCi · mL⁻¹ of Pu was typically observed in colloidal form (Wilson, 1991). In one set of experiments, it took about 780 d to replenish 300 mL of leachate. This rate of replenishment gives nucleation rates of about 77 pCi · d⁻¹. A spherical particle size of about 10⁻⁶ cm (10 nm) is assumed based on the pore size used for filtration. A value of $\sim 7 \times 10^3$, based on EQ3/6 calculations, was used for the C_s/C_o ratio assuming the formation of PuO₂ (Wilson, 1990b; Wilson and Bruton, 1989), and $\sim 10^{-2}$ for $e^{-G_d/RT}$ (Christian, 1975). The calculated γ values are in the range of 220 to 230 erg · cm⁻².

The γ values estimated for PuO₂ are smaller than typical values of about 1,000 erg · cm⁻² reported for dehydrated crystalline phases (Cherepanov, 1979). Small γ values have been proposed for the hydrated, amorphous, or polymeric phases (Cherepanov, 1979; Deanin, 1972; Shand, 1958). If small particles are ionized and dissolved ions are adsorbed, the values are expected to be less than 250 erg · cm⁻² for a stable particle suspension (Stol and de Bruyn, 1980). Small values also correspond to heterogeneous nucleation.

The critical number of ions necessary to form a stable particle, n_c , can be calculated using the relationship (Christian, 1975)

$$n_c = \left[\frac{(32 \pi \gamma^3 M^3)}{(3 \rho^2 \Delta g_v^3 N^2)} \right] \quad (3-9)$$

where

$$\begin{aligned} N &= \text{Avogadro number} \\ \Delta g_v &= \Delta G_v / N \end{aligned}$$

Using the values listed above, the values of n_c may be in the range from about 15 to 20, similar to values reported for other nucleation problems (Adamson, 1990). If γ (and n_c) decreases, the energetic barriers to nucleation decrease, and colloid particles will form more easily and become more stable. It should be noted that while these estimated values for γ and n_c are in general agreement with those for similar phenomena, they are based on a limited dataset, and should be used with caution.

In the formation of colloids, the phase with the lowest γ will be expected to form first, and will form spontaneously if γ has a very low or near-zero value. The process of colloid formation will continue until the consumption of dissolved ions reduces the level of supersaturation with respect to the particular phase being formed. At steady-state, there will be balance between complementary processes including nucleation, growth/flocculation, sedimentation, disintegration, and migration by groundwater. Alternatively, if the lowest γ values are still large, nucleation will be inhibited. For heterogeneous nucleation, the effective γ values will decrease. However, the model presented here for homogeneous nucleation is not sufficiently sophisticated to account for several complicating factors likely to be present

in a geologic repository, such as incorporation of Pu, Am, or Cm as solid solutions in U-bearing phases or Si colloids, or simultaneous formation of more than one phase. Experimental data on these complicating factors are not available for developing sophisticated models.

Nucleation of colloidal material should slow as the altered layer develops and dissolution of spent fuel is inhibited. However, if (i) the altered layer becomes unprotective or is disrupted or removed, and (ii) leachate is replenished or colloids are removed, further dissolution may occur, resulting in the formation of more colloids. Colloids may disintegrate because of radiation effects. Flocculation, adsorption, or growth may also lead to removal of colloids through settling in, or filtration by the geologic medium.

It should be noted that it is very difficult to determine true equilibrium solubility limits (Kim, 1986). This difficulty is because metastable polynuclei are present or the leachate is supersaturated. These calculations suggest the effects of these uncertainties in solubility limits. Depending on their magnitude, the implications of uncertainties in solubility limits on behavior of spent fuel may be significant.

Dispersion Processes

Dispersion involves the breakup of solid (or condensed) materials (Yariv and Cross, 1979). This process may involve spallation from the spent fuel surface, detachment of grains, or disintegration of grains or particles. Disintegration may result from an unstable or unprotective alteration layer. The loss of stability and protectiveness may be caused by: (i) alpha particle and recoil damage (Kim, 1986) and alpha radiolysis (Wang, 1981); (ii) stress generated during alteration, such as volume changes associated with phase changes and alteration; (iii) external stress and environmental variations, such as wet-dry cycles, temperature changes, local chemistry changes such as pH, and seismic activity; and (iv) microbial activities (Jones-Meehan et al., 1991). The effect of microbial activity on the formation of pseudocolloids is discussed in Section 4. The second type of disintegration results from preferential dissolution of grain boundaries (Wronkiewicz et al., 1992). The third type of disintegration results from radiation damage or oxidation of spent fuel (Matzke, 1992; Thomas et al., 1989; Stacey and Goode, 1978).

Dispersion processes and the subsequent disruption of the altered layer may lead to significant releases of colloids upon contact of water with spent fuel. However, insufficient experimental data exist to quantitatively evaluate the release of radionuclides in colloidal form. Uncertainties occur mainly in the understanding of: (i) colloid formation and accumulation; (ii) flocculation, growth, disintegration, or sedimentation; and (iii) transport by groundwater flow. Spallation may be induced by stresses associated with volume changes during formation of altered layers.

The strain energy associated with spallation can be calculated from volume changes on surface layer alteration using the elastic strain energy stored per unit volume as follows:

$$\epsilon = \frac{E}{2(1-2\nu)} \left(\frac{\Delta V}{3V} \right)^2 \quad (3-10)$$

where

$$\begin{aligned} E &= \text{Young's modulus} \\ \nu &= \text{Poisson's ratio} \\ (\Delta V/V) &= \text{volume expansion} \end{aligned}$$

The oxidation of UO_2 ($\rho = 10.96 \text{ g} \cdot \text{cm}^{-3}$) to U_3O_8 ($\rho = 8.40 \text{ g} \cdot \text{cm}^{-3}$) involves ~ 35.8 percent volume expansion (Thomas et al., 1989). Most of the strain energy is dissipated as heat. Assuming ~ 4 percent conversions of the strain energy to the energy associated with surfaces (Martin, 1985), $E \approx 145,000 \text{ MPa}$ (Schackelford, 1992) and $\nu \approx 0.3$ (Schackelford, 1992), the calculated value for the strain energy, ϵ , is about $10^9 \text{ ergs} \cdot \text{cm}^3$. The strain energy divided by surface energy per unit area, γ , gives the total surface area per unit volume (SA/V in cm^{-1}) created by the phase change. Assuming spherical particles, the average particle size can then be estimated. Assuming that γ for crystalline phases is about $1,000 \text{ erg} \cdot \text{cm}^{-2}$, the expected fractured particle size is approximately $3 \times 10^{-6} \text{ cm}$. This size is in the observed size range of U_3O_8 particles formed within U_4O_9 matrices, taking into account grain-boundary effects (Thomas et al., 1989; Stacey and Goode, 1978). It should be noted that this equation is for unit volume. The increase of altered volume with time will depend on the kinetics of alteration and the availability of water and O_2 . As in this example calculation, the volume expansion associated with the formation of uranosilicate (or schoepite) formation can be large. Therefore, observed colloids could possibly come from the spallation process of uranosilicates. Unlike the solid-state transformation in U_3O_8 , however, the formation of uranosilicates typically involves dissolution and precipitation, which may reduce the accumulated strain energy. Therefore, the use of Eq. (3-10) in uranosilicates may lead to an overestimation of strain energy or particle size.

Another possible dispersion mechanism is wear due to mechanical forces (Johnson et al., 1982). Such wear may be a complex function of parameters such as the wetted surface area of spent fuel, the groundwater flow rate, the mechanical load applied to the surface, and the toughness/hardness of the spent fuel and the secondary phases. However, there is a lack of quantitative data to evaluate the role of wear in colloid production, and the issue of transport of the particles away from the spent fuel surface is also problematic.

In addition to spallation and wear, colloid formation may also occur through intergranular dissolution that leads to the subsequent detachment of grains. This process has been observed during the UO_2 dissolution in drip tests in J-13 well water at 90°C (Wronkiewicz et al., 1992). The UO_2 drip tests for 238 weeks resulted in 20 to $40 \mu\text{g} \cdot \text{mL}^{-1}$ of uranium colloids. The process of grain detachment decreases as the altered layer develops and covers the UO_2 surface.

Pseudocolloid Formation

In addition to colloid formation through condensation or dispersion processes, pseudocolloids may also form. Groundwater in the vicinity of Yucca Mountain is generally known to have about 0.3 - to $1.4 \mu\text{g} \cdot \text{mL}^{-1}$ groundwater colloids in the size range of 0.03 to $1 \mu\text{m}$ (Kingston and Whitbeck, 1991). Groundwater colloids are composed mainly of silicate- or Fe-based minerals (U.S. Department of Energy, 1988; Kingston and Whitbeck, 1991). The amount of organic colloids reported (0.14 to $0.58 \mu\text{g} \cdot \text{mL}^{-1}$) is typically less than inorganic colloids in the Yucca Mountain site (U.S. Department of Energy, 1988). The presence of naturally occurring groundwater colloids supports the possibility of forming

pseudocolloids, by radionuclides released from spent fuel sorbing on groundwater colloids. The total amount of radionuclide sorbed to the colloidal phase, S , is approximated by (Domenico and Schwartz, 1990)

$$S = M_g K_d C \quad (3-11)$$

where

- M_g = mass of groundwater colloids
- K_d = the sorption coefficient for the groundwater colloid
- C = radionuclide concentration in leachate

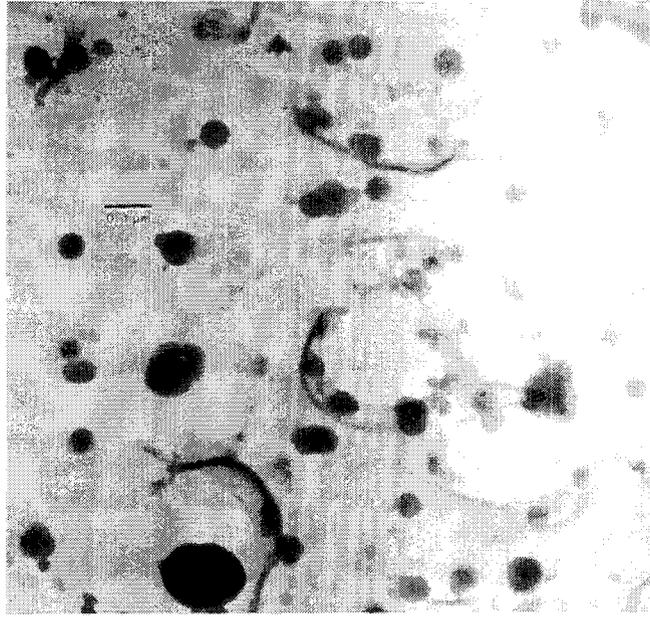
Equation (3-11) is only valid assuming instantaneous reversible linear sorption.

From batch sorption experiments using crushed tuff and J-13 water, the range of K_d values reported for Pu is about 100 to 30,000 mL · g⁻¹ (U.S. Department of Energy, 1988). Assuming $K_d = 10,000$ mL · g⁻¹, $C = 200$ pCi · mL⁻¹, and $M_g = 10^{-6}$ g · mL⁻¹, Eq. (3-11) yields a calculated value for S of 2 pCi · mL⁻¹ for Pu colloids. Organics typically have higher K_d values, but seem to be less abundant in the Yucca Mountain system. In addition to reversible sorption, pseudocolloids may also form by precipitation of insoluble phases on a pre-existing colloid surface. The precipitation of insoluble phases on a pre-existing colloid surface can be interpreted through heterogeneous nucleation. The uncertainties associated with distinguishing the sorption and precipitation mechanisms, in addition to the lack of information concerning interactions between organic molecules, inorganic colloids, and dissolved species make it difficult to quantitatively assess the significance of pseudocolloids in repository performance.

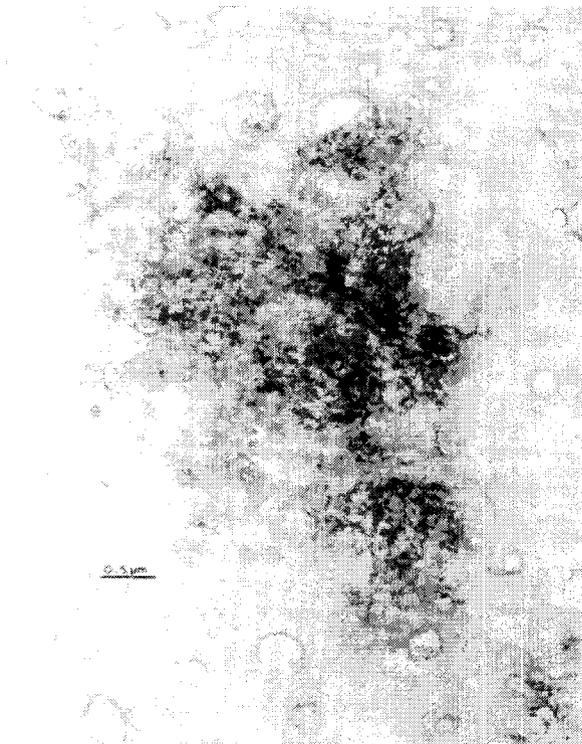
3.3.2 Vitrified (Glass) Wasteforms

Most of the general discussion in Section 3.3.1 about spent fuel dissolution is also relevant to vitrified (glass) wasteform leaching. The characteristics of colloid formation, however, will be different in the two cases. For example, iron oxyhydroxides or silicates form in glass leaching, instead of the uranosilicates observed in spent fuel dissolution. Although J-13 well water is commonly used as a starting leachate in most studies, the equilibrium leachate pH values observed for glass and spent fuel are quite different. This difference is likely to cause differences in the release rates of actinides from the two wasteforms, as actinide solubility depends on solution pH. As a result, additional experimental information related to the differences in the formation of colloids from spent fuel and vitrified wasteforms under geologic repository conditions is needed. Nevertheless, the mechanisms described above for colloid formation in spent fuel can be used for studying colloid formation from glass leaching (Ebert et al., 1993; Ahn et al., 1993). The processes of colloid formation, described earlier for spent fuel, have been reported in literature for vitrified wasteforms (Buck et al., 1993; Ebert and Bates, 1992; Muller et al., 1992; Shade and Strachan, 1986; Mendel, 1984). Direct evidence supporting the condensation and dispersion processes was also obtained in electron microscopy studies by Bates et al. (1992c) (Figures 3-4 and 3-5).

(²³⁹⁺²⁴⁰Pu and ²⁴¹Am were reportedly released as colloids in immersion tests of crushed simulated glasses, at 90 °C in J-13 well water (Ebert and Bates, 1992). In Figure 3-6 (Ebert and Bates,



(a)



(b)

Figure 3-4. Transmission electron microscopy (TEM) micrographs of particulate material isolated on a Holey Carbon TEM Grid: (a) colloids formed from solution and (b) material in solution spalled from the glass surface (Bates et al., 1992c)

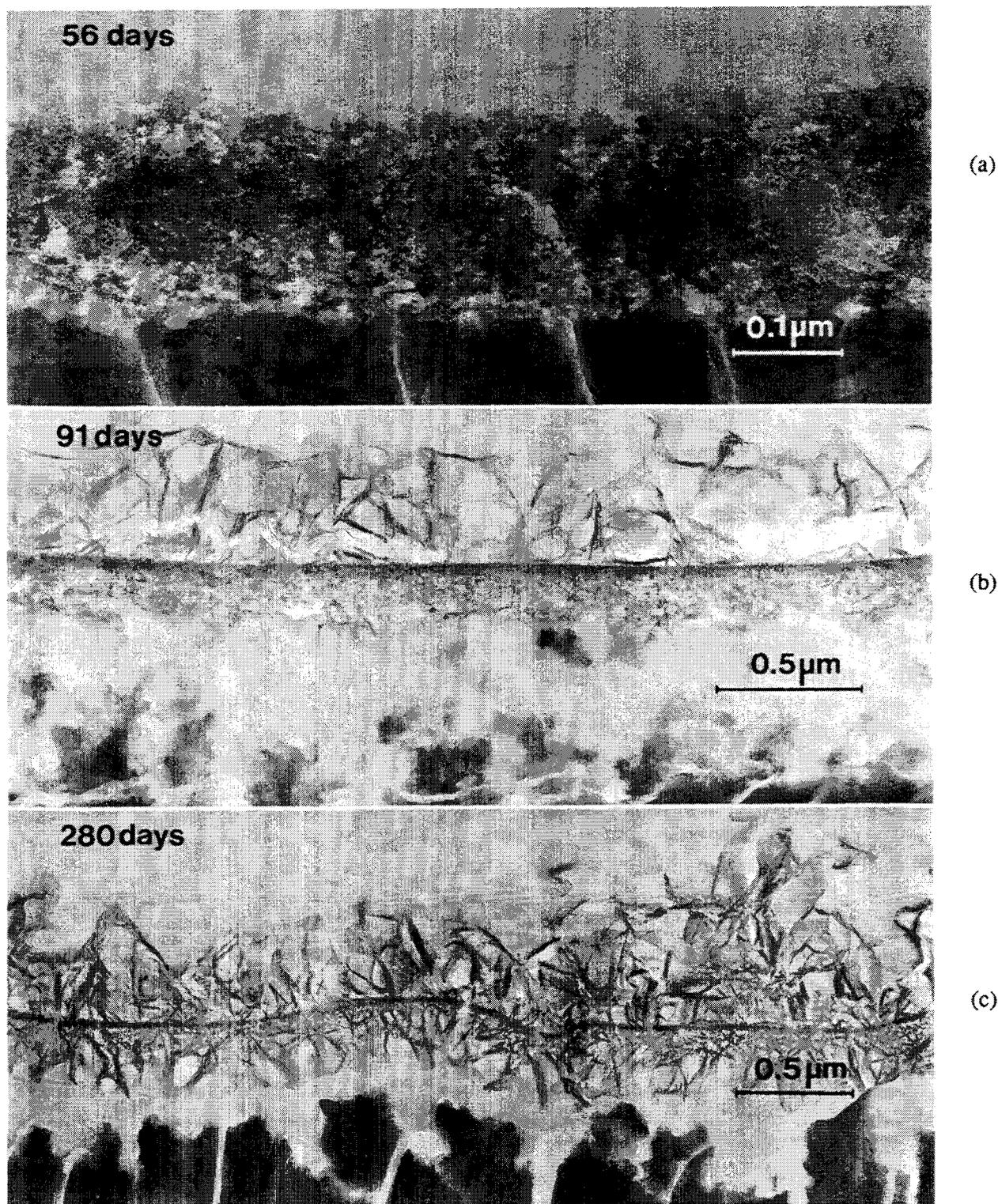


Figure 3-5. Brightfield electron micrographs of cross sections of glass reacted for (a) 56 d, (b) 91 d, and (c) 278 d, showing the formation of smectites (Bates et al., 1992c)

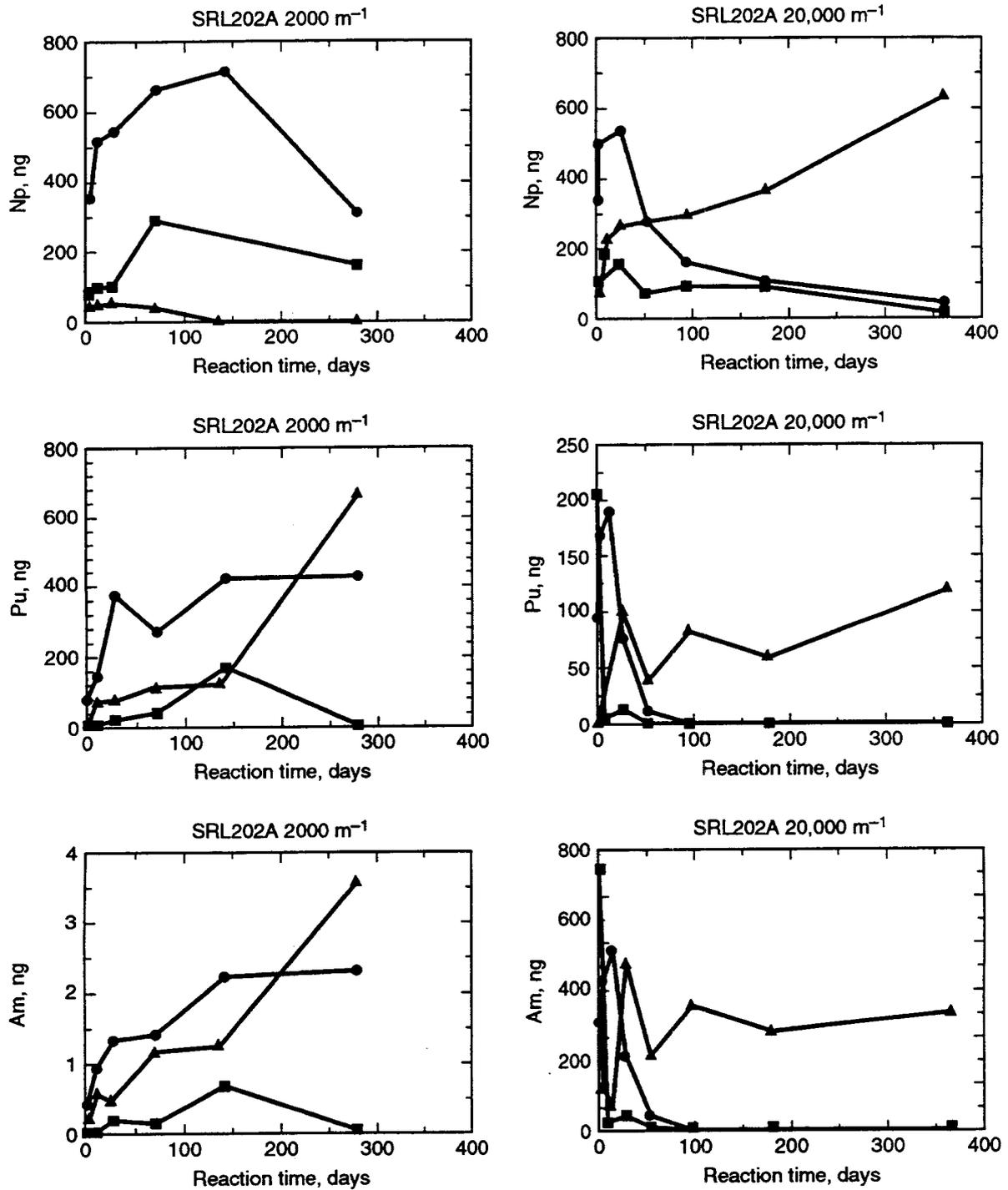


Figure 3-6. Mass action in (●) 0.45- μm filtrate, (■) 60- \AA filtrate, and (▲) acid soak solution for tests with SRL 202A glass at 2,000 m^{-1} (20 cm^{-1}) and 20,000 m^{-1} (200 cm^{-1}) in equilibrated J-13 groundwater at 90 °C (Ebert and Bates, 1992)

1992), actinide release is reported at two different values of specimen surface area (SA) to leachate volume (V) ratios. Approximately $910 \text{ pCi} \cdot \text{mL}^{-1}$ of $(^{239}+^{240})\text{Pu}$ and $\sim 640 \text{ pCi} \cdot \text{mL}^{-1}$ of ^{241}Am were released. At SA/V of $20,000 \text{ m}^{-1}$ (200 cm^{-1}), colloids (6 nm to $0.45 \mu\text{m}$) decrease as time increases. This decrease is attributed by the authors to high pH and ionic strength. At the lower SA/V of $2,000 \text{ m}^{-1}$ (20 cm^{-1}), colloids appear to be stable.

Shade and Strachan (1986) used MCC-3 tests (immersion with slow agitation) using crushed simulated (nonradioactive) vitrified wasteform in deionized water and silica water at $90 \text{ }^\circ\text{C}$. Based on the amount of silica released, approximately $5,000 \text{ pCi} \cdot \text{mL}^{-1}$ of Am and Pu colloids are estimated to be released. This estimate is based on composition of glass (Bates et al., 1993). Agitation in the MCC-3 tests may have prevented particle settling, leading to higher colloid concentration than in static tests. However, the MCC-3 tests and static tests show similar amounts of colloids (Ebert and Bates, 1992c). Under drip test conditions of J-13 well water at $90 \text{ }^\circ\text{C}$, Bates et al. (1992b) have shown that Am-241 and (Pu + Am) are released almost 100 percent in colloidal form, whereas Np was found predominantly in solution (Table 3-1). Approximately $9.7 \times 10^3 \text{ pCi} \cdot \text{mL}^{-1}$ of Pu and Am are released.

Table 3-1. Drip test results of simulated high-level waste glass with J-13 groundwater at $90 \text{ }^\circ\text{C}$ (adapted from Bates et al., 1992b)

Fraction	Np		Pu + Am	
	#1	#2	#1	#2
	(10^{-8}g)		(10^{-10}g)	
Initial	17.4	6.0	108	1087
Delayed	16.3	—	119	—
	Percent Passage			
1.0 μm	100	100	4	0.6
0.40 μm	100	100	4	0.6
0.10 μm	100	100	3	0.4
0.05 μm	85	100	2	0.3
0.015 μm	85	72	2	0.3
0.003 μm	70	70	1	0.01
0.001 μm	70	65	0.05	0.00

The leaching rate of Si from the vitrified wasteform has been suggested as a principal factor in colloid release because the silica (SiO_2) matrix is the main constituent of the wasteform (Avogadro and de Marsily, 1984). Experimental evidence suggests that the flocculation or the growth of colloids occurs only at large values of SA/V, high ionic strength, or at high pH in immersion tests. It is uncertain if the colloid material formed during glass alteration will be removed from the wasteform surface and will settle out under repository conditions.

4 FIELD EVIDENCE FOR COLLOIDS AND THE POTENTIAL INFLUENCE OF NATURAL SYSTEMS ON SORPTION, FILTRATION, AND TRANSPORT OF COLLOIDS

In most countries, deep geologic disposal of HLW has been selected as the method of choice. Most potential repository sites in countries around the world are located in hydrologically saturated environments. In the United States, however, the candidate repository site currently under evaluation is in an arid region and is hydrologically unsaturated. The proposed formation for HLW emplacement is approximately 300 m below the ground surface and approximately 250 to 300 m above the water table. This section briefly summarizes the salient geologic setting and geochemical features of the Yucca Mountain repository site, in Nevada, currently under investigation. Literature data relevant to groundwater colloids and potential transport of radionuclides via colloids are also provided.

4.1 YUCCA MOUNTAIN GEOLOGIC SETTING

The oldest volcanics in the vicinity of Yucca Mountain and the NTS are dated at 29 million years (m.y.) (part of the Horse Spring Formation, 24–37 m.y.), and all subsequent Cenozoic volcanic episodes of the region are represented. Yucca Mountain is primarily composed of Tertiary volcanics. The bulk of the igneous activity began with the eruption of rhyolitic to dacitic, welded to nonwelded tuffs at about 16 m.y. from calderas to the north (U.S. Department of Energy, 1988), and culminated in the eruption of the Thirsty Canyon Tuff from the Black Mountain Caldera at about 7 m.y. This interval includes the Calico Hills, and Paintbrush Tuffs, and the Timber Mountain Tuff, which overlies them on the eastern flank of Yucca Mountain. Tertiary units at Yucca Mountain decrease in thickness from west to east.

In the Yucca Mountain area, Precambrian outcrop is limited to gneiss and schist in the Bullfrog Hills to the northwest, and to quartzite, sandstones, and shales of the Johnnie Formation and Sterling Quartzite in the Spring Mountains to the southeast (McKague et al., 1989). The Paleozoic section extends from the Cambrian Wood Canyon Formation to the southeast near Lathrop Wells, upwards through the Permian Timpipah Limestone at Syncline Ridge to the northeast (Cornwall, 1972), for a total thickness of ~9,000 m (McKague et al., 1989). Precambrian and Paleozoic rocks do not crop out in the exploratory block, but they are believed to underlie the Tertiary volcanics of Yucca Mountain (U.S. Department of Energy, 1988; Mattson et al., 1989). To date, however, a drill core along the mountain crest (e.g., USW-G1) has penetrated to 1,800 m without leaving the volcanics. Paleozoic carbonate (Silurian Lone Mountain Dolomite and Roberts Mountain Formation) has only been encountered in a drill hole about 3 km to the southeast of the proposed repository site at a depth of about 1,200 m (Carr et al., 1986).

Two main structural features are associated with the Cenozoic Era. The first includes caldera formation and extensional faulting associated with the eruption of the silicic tuffs (6 to 34 m.y.). This feature is largely confined to Nye, Esmeralda, and Lander Counties, although there are other scattered locations throughout the state. Caldera formation is closely associated with the Yucca Mountain area, where a cluster of calderas from Mount Helen (> 14 m.y.) through Timber Mountain (~ 11 m.y.), and ending with the Black Mountain Caldera (~ 7 m.y.) erupted the thick tuff sequence that is being considered for the repository (Hannon and McKague, 1975).

The second and dominant structural feature of the Great Basin is the normal faulting associated with Basin and Range extension, beginning at about 17 m.y. and continuing into historic time. Three fault geometries have been associated with Basin and Range extension: high-angle normal faulting, listric normal faulting, and low-angle extension, all of which may be present in the vicinity of Yucca Mountain (U.S. Department of Energy, 1988). The Yucca Mountain structural block itself has been tilted to the east along a series of north-trending high-angle Basin and Range normal faults. Consistent with the Basin and Range geographic province, thick sequences of Tertiary and Quaternary sediments fill the basins and drainages between extensional mountain ranges in the region.

The proposed repository will be constructed in the hydrologically unsaturated zone about 250 to 300 m beneath the ground surface and some 200 to 400 m above the static water level (SWL) (U.S. Department of Energy, 1988). The candidate host rock is the Topopah Spring Member of the Paintbrush Tuff. The cooling units of the tuffs are divided into welded vitric layers and nonwelded layers with varying amounts of lithophysae. In the nonwelded layers, much of the original glass has devitrified into a high-temperature feldspar + silica mineral assemblage. The middle and lower tuffs have been altered to a zeolite-clay assemblage; the contact between the zeolitized tuffs and the unaltered tuffs is thought to represent the highest level reached by the SWL since initially receding more than 11 m.y. ago (Levy, 1992).

4.2 HYDROGEOLOGY

The hydrogeology of the saturated zone in the Yucca Mountain region is divided among three basic types of units (with decreasing age and depth): the Paleozoic carbonates, Tertiary tuffs and lavas, and Tertiary and Quaternary basin fill. Intercrystalline porosity and permeability in the carbonates and in welded tuffs and lavas are typically low, and most of the permeability is contributed by fractures and faults (Winograd and Thordarson, 1975). Less fractured units tend to act as aquitards to flow in the fractured aquifers (Figures 4-1 and 4-2). Flow in the bedded tuffs and much of the basin fill, however, is controlled by primary porosity and permeability. Fracturing in these units is low and contributes little to regional groundwater flow. Recharge in the semiarid climate of Yucca Mountain is likely to occur from winter storms in the surrounding mountains and from intermittent flow in the washes and canyons. Major discharge areas are found in Sarcobatus Flat to the northwest of Yucca Mountain and Amargosa Desert/Ash Meadows to the southwest. The ultimate discharge point is in Death Valley. Perched groundwaters are found in the units, and spring discharge is found from some of the less fractured aquitards. Flow through the unsaturated zone is still poorly understood and may occur by episodic flow along fractures.

4.3 NATURALLY OCCURRING COLLOIDS IN THE YUCCA MOUNTAIN VICINITY

Colloids have been reported from a few wells in the vicinity of Yucca Mountain. The amount of suspended matter is generally small, on the order of 1 to 10^{-2} mg · L⁻¹ (U.S. Department of Energy, 1988; Kingston and Whitbeck, 1991). Analysis shows the groundwater colloids to be made up of clays, feldspars, quartz, and organics—materials that are known to sorb radionuclides. Initial porosimetry data (Daniels et al., 1982) suggest that more than 50 percent of the matrix pores in the tuffs are less than 100 nm (less than 50 nm in some cases), too small to allow significant colloid transport through the matrix (U.S. Department of Energy, 1988). Field studies conducted in tuffs at the NTS indicate that colloids are retarded relative to the migration of a conservative tracer. Fracture apertures at Yucca

Stratigraphic Unit		Geohydrologic Unit (Where Unsaturated)
Alluvium		Alluvium (QAL)
Paintbrush Tuff	Tiva Canyon Member	Tiva Canyon Welded Unit (TCw)
	Yucca Mountain Member	Paintbrush Tuff Nonwelded Unit (PTn)
	Pah Canyon Member	
	Topopah Spring Member	Topopah Spring Welded Unit (TSw)
		Calico Hills Non-Welded Unit (CHn)
Tuffaceous Beds of Calico Hills		<div style="display: flex; align-items: center; justify-content: center;"> <div style="border: 1px solid black; padding: 5px;">Vitric (CHnv)</div> <div style="border: 1px solid black; padding: 5px; margin-left: 20px;">Zeolitized (CHnz)</div> </div>
Crater Flat Tuff	Prow Pass Member	
	Bullfrog Member	Crater Flat Unit (CFu)

Note: Figure Not to Scale

Figure 4-1. Stratigraphic and geohydrologic units in the Yucca Mountain exploratory block. The repository horizon is the Topopah Spring Member. The diagonal dashed line represents the static water level (adapted from U.S. Department of Energy, 1988)

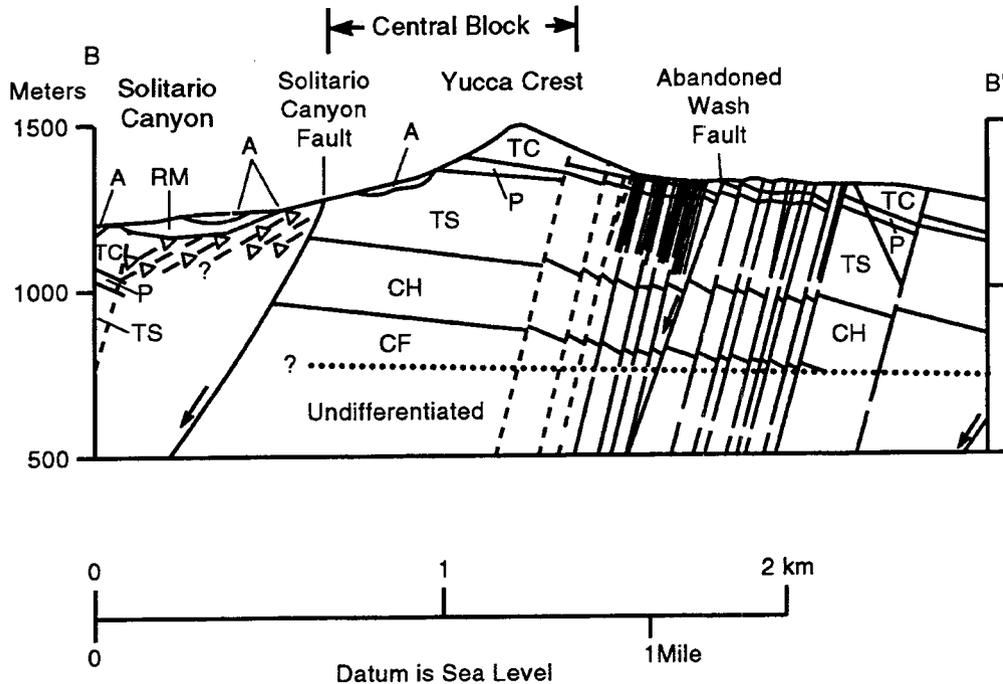


Figure 4-2. East-west cross section of Yucca Mountain looking to the north. The horizontal dotted line shows the approximate location of the static water level. Unit symbols are: A—Alluvium; RM—Rainier Mesa member of the Timber Mountain Tuff; TC—Tiva Canyon Welded Unit; P—Paintbrush Nonwelded Unit; TS—Topopah Spring Welded Unit; CH—Calico Hills Nonwelded Unit; CF—Crater Flat Unit (adapted from Scott and Bonk, 1984)

Mountain, however, are large enough to allow colloid transport by fracture flow should the colloids be formed or deposited in or near fractures.

4.3.1 Groundwater (Natural) Colloids

Buddemeier and Hunt (1988) studied colloidal transport in hydrologically saturated fractured tuff and lava at the site of the Cheshire event on the NTS. Water samples were filtered from 3 nm to 1 μm . Essentially all the transition (Mn, Co) and lanthanide (Ce, Eu) radioelements were associated with the colloidal fraction. For the 3- to 50-nm fraction, colloid mass concentration in the formation was about $4.5 \text{ mg} \cdot \text{L}^{-1}$. Although this concentration is higher than the J-13 waters (10^{-3} to $10^{-5} \text{ g} \cdot \text{L}^{-1}$), Buddemeier and Hunt (1988) report relatively high pumping rates ($\sim 120 \text{ L} \cdot \text{min}^{-1}$), raising the possibility of increased suspension of particulates due to hydrodynamic shear forces. In the detonation cavity, colloid concentration was higher, ranging from 10.1 (3 to 50 nm) to 63 (6 to 450 nm) $\text{mg} \cdot \text{L}^{-1}$. X-ray diffraction analyses of a sample from the detonation cavity indicated that the bulk of 3- to 50-nm ultrafiltrate was dominated by quartz, (Ca, K) feldspars, with a possible clay fraction of about 10 percent. Buddemeier and Hunt (1988) also reported that the groundwaters in the Pahute Mesa drainage in the

northern part of the NTS contain 0.8 to 6.9 mg · L⁻¹ particles > 30 nm, and one spring on the NTS contains about 16.4 mg · L⁻¹ particles in the 30- to 400-nm fraction.

Since there is no flowing water in the unsaturated zone at the proposed repository site, Well J-13 in Jackass Flat to the east of Yucca Mountain was sampled for natural colloids (Kerrisk, 1987; U.S. Department of Energy, 1988). Pumping rates of about 1 L · min⁻¹ were used during sampling; water was prefiltered for particles > 10 μm and then filtered through a series of 400-nm membrane and 5-nm hollow fiber filters. Filtering 9,300 L of water through the membrane filters yielded about 2.7 × 10⁻⁵ g · L⁻¹ of particulate material. The bulk of the material was retained by the 400-nm filter assemblies, and the 5- to 400-nm filtrate accounted for less than 1 percent of the total yield. Analysis of the 400-nm to 10-μm fraction with SEM and emission spectroscopy (EM) indicated a composition dominated by Si-Fe-Ca, with minor Al, while the 5- to 400-nm fraction was predominantly Na-Si with minor amounts of Ca and Fe. Levy (1992) reports evidence for relict gels and possible colloids lining fractures and filling some of the vugs in the zeolitized nonwelded tuffs at Yucca Mountain. Planar layering is characteristic of these deposits of cristobalite and zeolite, suggesting that gels (and possibly colloids) settled out in these vugs, which acted as traps for downward moving waters during the diagenetic and hydrothermal alteration of the tuffs.

4.3.2 Real- or True-Colloid Formation

In addition to natural colloids, several of the radionuclides predicted to be important in repository performance (Kerrisk, 1985) are known to form true radiocolloids through hydrolysis, polymerization, and crystallization (Patera et al., 1990). Oloffson et al. (1982a, b; 1985) used centrifugation to examine the formation of true radiocolloids for Am, Np, and Pu in NaClO₄ solutions under a variety of pH, ionic strength, and radionuclide concentrations. When centrifuged at high speed (27,000 g), only particles smaller than 50 nm could remain in solution. Both Am and Pu exhibited appreciable colloidal formation at high pH, possibly as Am(OH)₃ and Pu(OH)₄, respectively. In contrast, the centrifugable fraction of Np was negligible, except at pH > 10 for high ionic strength solutions (1 M NaClO₄). Kim et al. (1987b) also proposed the generation of centrifugable Am true radiocolloids in experiments performed with natural groundwaters containing significant amounts of DOC. Hobart et al. (1989) reported on the preparation and analysis of Pu(IV) colloidal suspensions, and observed that the redox potentials of the colloids differed significantly from those predicted for dissolved Pu⁺⁴ ions. Using autocorrelation photon spectroscopy, Rundberg et al. (1988) determined that the diameter and density of ²⁴²Pu colloids were 2.9 ± 0.2 nm and 9.0 g · cm⁻³, respectively. Rundberg et al. (1988) also observed that a ²³⁹Pu colloid formed in the experiment remained stable at 180 nm for over 2 yr.

In contrast, several studies (Avogadro and de Marsily, 1984; Laul et al., 1985; Maiti et al., 1989) did not observe colloid formation for a number of radionuclides in synthetic brines down to particle sizes of 15 nm. This lack of colloid formation is to be expected in that hydrolysis is inhibited at high ionic strengths (i.e., high concentrations of dissolved solids). Based on electrostatic double layer (EDL) theory, high ionic strength or high valence collapses the diffuse double layer surrounding the charged ions in solution. Because dispersion of charged colloids is favored by electrostatic repulsion related to a thick double layer, high ionic strengths (thin double layers) tend to favor aggregation. This phenomena tends to hamper Brownian motion of small particles and reduces particle collisions. The reduced number of collisions in turn inhibits the polymerization of mononuclear hydroxyl compounds. The importance of real colloids in the relatively dilute conditions prevalent at Yucca Mountain (ionic strength ≈ 10⁻³ m for J-13) is not understood completely.

4.3.3 Organic Colloids

Organic material is also reported in J-13 well water (Means et al., 1983; U.S. Department of Energy, 1988). Total organic carbon (TOC) is reported at $0.14 \pm 0.05 \text{ mg} \cdot \text{L}^{-1}$, and compounds greater than 1,000 MW make up more than 50 percent of the material. Based on these analyses, there seems to be at least some natural colloidal matter suitable for the formation of pseudocolloids. Minai et al. (1992) identified $2.7 \text{ meq} \cdot \text{g}^{-1}$ for the fulvic acid fraction of TOC, and $4.6 \text{ meq} \cdot \text{g}^{-1}$ for the humic acid fraction.

Based on the literature review, it is concluded that additional work is necessary to fully characterize the natural colloids in the Yucca Mountain system, to understand the association of important radionuclides with these materials, and to determine the extent to which suspended particles can be transported through the different geologic units.

4.4 SORPTION/FILTRATION AND TRANSPORT OF COLLOIDS

This section provides a review of the literature-reported studies on sorption, filtration, and transport of colloids. The emphasis is on actinides of interest to the long-term performance of a geologic repository such as Am, Np, and Pu. Data from real colloids and pseudocolloids in a number of different groundwaters are examined.

4.4.1 Sorption on Colloids

In the context of HLW disposal, colloids are only significant to the extent to which they influence radionuclide transport through the geologic setting. For this reason, only if radioactive elements are associated with the colloidal phase either through the formation of true colloids or the sorption of radionuclides on colloids already present in the groundwater are they factored into radionuclide transport calculations. Traditional approaches to modeling pseudocolloid migration are to assume an equilibrium, linear sorption isotherm (e.g., Harvey and Garabedian, 1991). Smith (1993b) indicated that in this type of model, radionuclide migration would not be significantly enhanced by colloids. The incorporation of irreversible sorption onto colloidal particles does, however, suggest that the rate of radionuclide transport is strongly dependent on the efficiency of colloid transport and filtration in the medium of interest (Smith, 1993b). The following subsection briefly summarizes is a brief summary of the surface characteristics of a variety of the more common colloidal material found in a natural groundwater system and their potential for sorption during transport in a geologic environment.

4.4.1.1 Sorption on Groundwater Colloids—Inorganics

Colloids of inorganic materials in a geologic repository include oxides and oxyhydroxides, clays, and micas, silicates and aluminosilicates, and carbonates.

Oxides and Oxyhydroxides

Precipitated oxides and oxyhydroxides of metals such as Fe, Al, Ti, and Si are common in groundwater systems. Reactive surface areas can be high for the amorphous forms of these minerals (e.g., A_{SP} for synthetic $\text{Fe}(\text{OH})_3$ is reported from about 150 to $800 \text{ m}^2 \cdot \text{g}^{-1}$; Dzombak and Morel, 1990), suggesting the potential importance of these minerals as a sorbent phase, especially for small particles like

colloids. In addition, the potential for forming a sorptive coating on less sorptive particles such as quartz or feldspar suggests an additional role for these minerals in colloid transport (Robert and Terce, 1989).

Titration experiments with (hydr)oxides indicate that surface charge is a complex function of pH, ionic strength, and solution chemistry (Kent et al., 1988; Davis and Kent, 1990; Hayes et al., 1990; Turner, 1993). As a means of explaining this behavior, EDL theory postulates that the (hydr)oxide-water interface is composed of amphoteric surface hydroxyl ($\text{Me} \equiv \text{OH}^0$) groups that can act either as an acid or as a base. Because the protonation or deprotonation of these sites (i.e., the addition or subtraction of a proton as H^+) depends on the dissociation of the water molecules, the pH of the solution determines the surface charge of the particle (Kent et al., 1988). At low pH values, there is a surplus of H^+ ions at the surface, and the particle exhibits an overall positive charge ($\text{Me} \equiv \text{OH}_2^+$ sites are dominant). As pH increases, H^+ activity is low, and deprotonated sites (i.e., $\text{Me} \equiv \text{O}^-$) become more abundant at the oxide-water interface, giving the particle a negative charge. At some intermediate pH value, called the pH of the zero point of charge (pH_{ZPC}), the positively and negatively charged sites balance and the particle exhibits zero net charge. From electrostatic repulsion, anions will tend to adsorb on $\text{Me} \equiv \text{OH}_2^+$ sites, while cations will be adsorbed at deprotonated $\text{Me} \equiv \text{O}^-$ sites. This process leads to the formation of a sharp sorption edge where sorption of cations increases (as the number of $\text{Me} \equiv \text{O}^-$ sites increases) from zero to nearly 100 percent over a relatively narrow pH range. For anions such as SeO_4^{2-} , the reverse is true; sorption typically decreases in a gradual fashion with increasing pH (Balistrieri and Chao, 1990).

A number of experimental studies have demonstrated the affinity of key radionuclides for oxyhydroxides and silicate minerals (Figure 4-3). Uranium exhibits pH-dependent sorption on Fe (hydr)oxides (Hsi and Langmuir, 1985; Tripathi, 1984; Venkatamarani and Gupta, 1991). Sorption of Pu (Sanchez et al., 1985), Th (LaFlamme and Murray, 1987; Hunter et al., 1988), and Np (Girvin et al., 1991) on Fe oxyhydroxides shows sorption edges over a pH range from 3 to about 6. Limited experimental data (Hsi, 1981) suggest that cation competition (Ca, Mg) has little effect on uranium sorption behavior. The introduction of $\text{CO}_2/\text{CO}_3^{2-}$, however, induces a desorption edge at higher pH (Figure 4-4). Actinide sorption on different polymorphs of Al_2O_3 (Prikryl et al., 1993; Righetto et al., 1988, 1991) and TiO_2 (Lieser and Thybusch, 1988; Venkatamarani and Gupta, 1991) exhibits a similar behavior. This behavior is relevant to conditions at Yucca Mountain, where the unsaturated zone is open to CO_2 (Thorstenson et al., 1990), and water from J-13 is predominantly a sodium bicarbonate solution (U.S. Department of Energy, 1988). Recent efforts have focused on developing uniform approaches to modeling the complex sorption behavior of actinides (e.g., Turner, 1993).

In addition to oxides and oxyhydroxides, natural colloids in the subsurface are typically composed of minerals similar to the aquifer material (Degueudre, 1993). Since these minerals are likely to be the platform for forming pseudocolloids, it is appropriate to discuss their sorption behavior in a general sense.

Clays and Micaceous

Sheet silicates such as clay and mica minerals are found in a wide variety of geologic environments, occurring either as primary minerals or as secondary replacement and weathering products. Because of a permanent negative charge due to substitution of Al^{3+} for Si^{4+} , and the large surface area resulting from their layered structure, sheet silicates can have a high cation exchange capacity (Kent et al., 1988). The edge sites (perpendicular to the silicate layers) also exhibit a surface charge that varies as a function of pH similar to that described above for oxides and oxyhydroxides. Mineralogically, clays

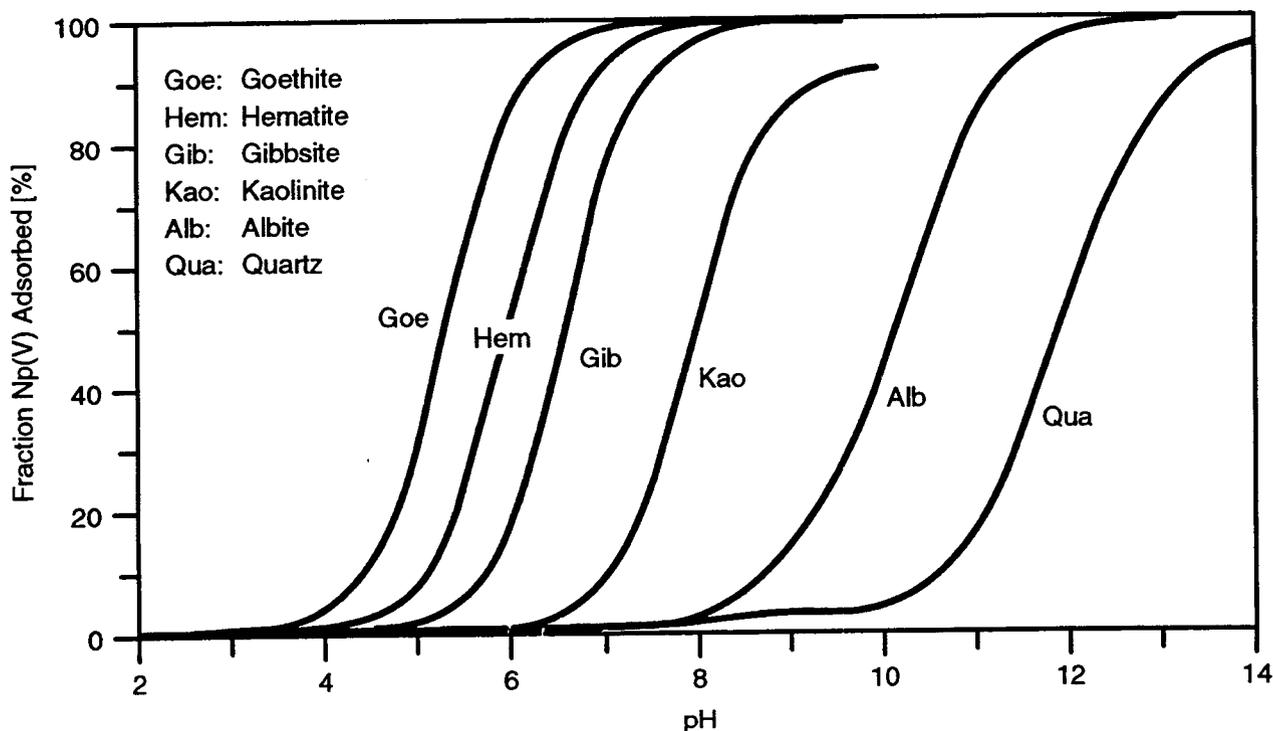


Figure 4-3. Predicted adsorption of Np(V) as a function of pH onto different minerals ($Np_T = 1.1-1.3 \times 10^{-7}$ M). A triple-layer surface complexation model (Davis and Kent, 1990) was used assuming a total site concentration for each mineral of 5×10^{-4} M (adapted from Kohler et al., 1992). Observed pH values at Yucca Mountain typically range from about 6 to 9.

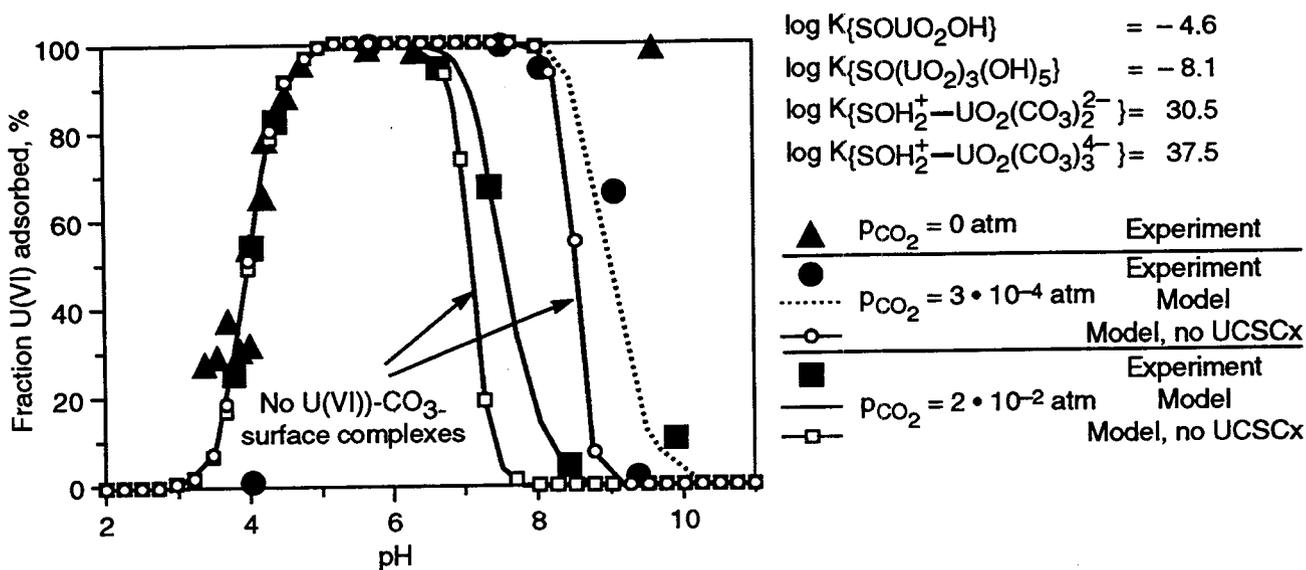


Figure 4-4. Uranium sorption on goethite ($U_T = 10^{-6}$ M). Model predictions using a triple-layer surface complexation model (Davis and Kent, 1990) (adapted from Kohler et al., 1992).

are divided into four groups: the kaolinite group, the smectite group, the illite group, and the vermiculite group (Deer et al., 1966). Micaceous minerals include primary rock-forming minerals like biotite, muscovite, and paragonite. Other sheet silicates include chlorite and pyrophyllite. Smectite, vermiculite, and some kaolinite group clays expand upon interaction with water or organic fluids. This expansion can change the interlayer spacing and affect both the degree to which radionuclides can penetrate the interlayer exchange sites and sorb onto clays and the extent to which colloidal particles can be transported in a porous or fractured medium (Nielsen et al., 1986; Goldberg et al., 1991). Sorption on clays is a function of surface charge and specific surface area (Kent et al., 1988). Batch experiments (Comans et al., 1991) indicate that the sorption of Cs^+ ions on illite clays is generally higher in a Ca-rich environment relative to a K-rich environment. This higher rate of Cs^+ sorption appears to be due to the fact that the higher charge of Ca^{2+} relative to K^+ leads to hydrated ions that tend to prop open the layered structure, making energetically favorable interlayer sites more accessible to the sorbing cation. Sorption experiments on Am^{3+} (Stammose and Dolo, 1990), UO_2^{2+} (Payne et al., 1992; Della Mea et al., 1992), NpO_2^+ (Nakayama and Sakamoto, 1991; Righetto et al., 1991), and Th^{4+} (Riese, 1982) demonstrate that actinides exhibit pH-dependent sorption behavior on different clays and micaceous minerals. This behavior suggests that sorption of these radioelements is controlled by the edge sites in the crystal structure.

Silicates and Aluminosilicates (Quartz, Feldspar, Amorphous Silica, Zeolites)

Silicates are typically among the most abundant minerals in a geologic environment. Although the surface area of these minerals is generally small, the abundance of these minerals makes them important from the point of view of sorption and transport. Simple SiO_2 (quartz, amorphous silica) behaves as other oxides, with a variable surface charge due to the acid/base behavior of surface hydroxyl groups. Although feldspar involves the substitution of Al^{3+} for Si^{4+} , it does not exhibit a fixed charge. Feldspar can be treated as a combination of site types (e.g., $\equiv\text{AlOH}^\circ$ and $\equiv\text{SiOH}^\circ$), each exhibiting a pH-dependent surface charge that varies as a function of the protonation and deprotonation of surface hydroxyl groups (Kent et al., 1988; Davis and Kent, 1990). Minerals such as zeolites exhibit a fixed charge and behave more like the interplanar exchange sites in clays. The negative charge developed by substitution of Al^{3+} for Si^{4+} is compensated by Na^+ , K^+ , Ca^{2+} , and Mg^{2+} in the intracrystalline exchange sites. Sorption is typically by way of ion exchange in the intracrystalline sites (Davis and Kent, 1990), particularly for the alkaline and alkaline earth elements such as Cs^+ and Sr^{2+} , but there also appears to be a component of pH-dependent surface charge as well (Pabalan et al., 1993; Pabalan and Turner, 1993). Moulin et al. (1992) studied the adsorption of Am^{3+} , NpO_2^+ , and UO_2^{2+} on silicate colloids and observed a dependence on both pH and radioelement oxidation state.

Carbonates

In carbonate aquifers, calcite and dolomite are reported as colloids and suspended particles in natural systems. The surface charge of these minerals is dominated by the balance between the dominant cation (Ca^{2+} or Mg^{2+}) and the carbonate anion (CO_3^{2-}). For this reason, surface charge is a complex function of pH, solution chemistry, and $p(\text{CO}_2)$. Recent modeling efforts have focused on adapting surface complexation models to describe sorption at the carbonate/water interface (e.g., van Cappellen et al., 1993).

4.4.1.2 Sorption on Groundwater Colloids—Organics

The formation of pseudocolloids by complexation or binding of radionuclides on microbes and humic colloids is essentially the same process. These pseudocolloids involve complexation with available

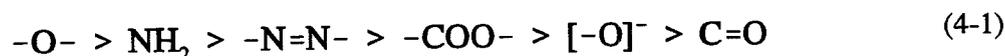
functional groups. This complexation process can also enhance the solubility of radionuclides. Kim (1991) measured the concentration of a variety of M(III) and M(IV) metals in groundwaters and noted that concentrations are a linear function of the DOC concentration. For example, studies of Kohler et al. (1992) indicate that the presence of EDTA in millimolar concentrations (10^{-4} to 10^{-3} M) can significantly reduce the amount of Np(V) sorbed on kaolinite. EDTA concentrations of the order of 10^{-6} M, however, have only a slight effect on the sorption behavior (Figure 4-5).

Microorganisms

A wide variety of microorganisms may be found in groundwater systems. Aerobic and anaerobic bacteria may both be found in the subsurface. In addition to affecting biodegradation, these organisms may affect the species of metals (radionuclides) in a variety of ways:

- (i) Binding the metal species to the surface of the cell
- (ii) Transforming the metal species to another by redox reactions or complexation with organic ligands
- (iii) Precipitating the metal in an insoluble form (Chappelle, 1993)

Biological surfaces contain a number of functional groups that chelate dissolved metal species. The affinity of the binding sites for metals is not equal from one site to the other. Metals will bind to the functional groups with high affinity first (Xue et al., 1988). The affinities of the functional groups for metal ions are given here in decreasing order (Thurman, 1985a):



Gonçalves et al. (1987) have observed that the affinity of metals for microbial surfaces is a function of pH, ionic strength, and competing ion concentrations. Under similar chemical conditions, the affinity for metals such as Cu, Pb, and Zn by microorganism surfaces is greater than by inorganic colloids such as goethite. The tendency to form complexes will decrease with increased loading (metal species concentration on the surface) (Xue et al., 1988).

Dissolved Organic Carbon

A variety of studies has been conducted to determine the complexation or binding behavior of metals by humic substances (Ephraim et al., 1989; Kim et al., 1991; Higgs et al., 1992; Tipping, 1993). Similar to the surfaces of microorganisms, there is a heterogeneity of binding strength among sites on the humic and fulvic acids. The strong complexing sites are few in number relative to the weak complexing sites (Carlsen, 1989). Multidentate complexation causes humic colloids to have a strong affinity for higher oxidation states ($Z \geq +3$) (Kim, 1991). Binding of actinides by humic substances follows the sequence:

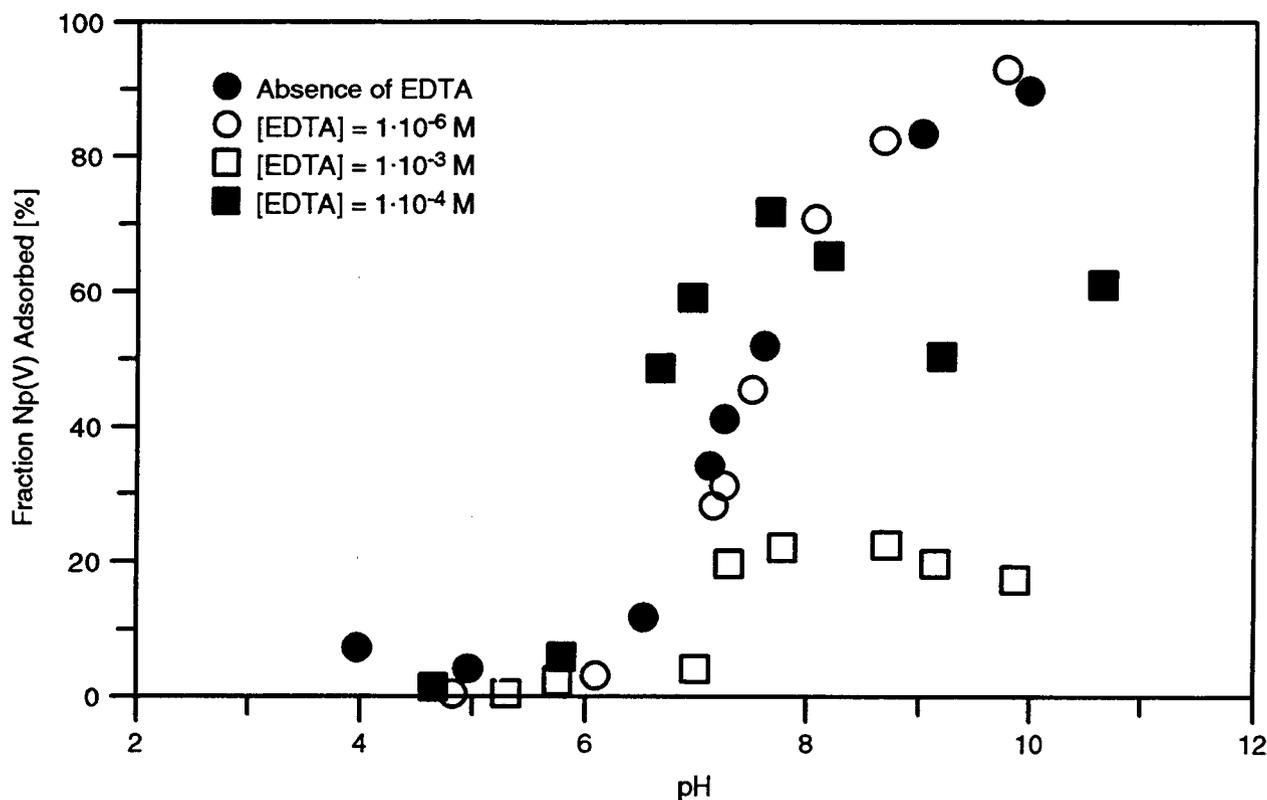
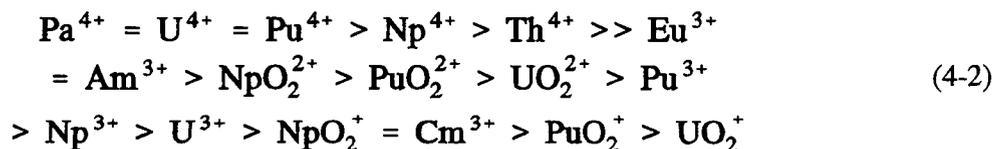


Figure 4-5. Np(V) sorption on kaolinite in the presence of different concentrations of ethylenediaminetetraacetic acid (EDTA). $Np_T = 1.2 - 1.3 \times 10^{-7}$ M (after Kohler et al., 1992)



In general, cation charge, pH, ionic strength, the relative concentrations of humic material and competing cations, as well as the concentration of anionic species such as phosphate (Andersson, 1988) will affect the extent of humate-radionuclide complex formation. For example:

- (i) The binding of UO_2^{2+} by fulvic acids decreases with increasing pH because of UO_2^{2+} -carbonate complex formation (Higgo et al., 1992)
- (ii) Th(IV) and Pu(IV) form such highly stable complexes with humates that these ions do not complex with carbonate, even at elevated pH (Carlsen, 1989)

- (iii) At low Eu^{3+} concentrations, the interaction constant for Eu^{3+} increases with pH because of increased dissociation of humic material (Maes et al., 1991)

The complexation of actinides by humic substances is reversible. However, with time, adsorbed cations may become more tightly bound by the humic material (Clark and Choppin, 1990). Real colloids of actinides can also be sorbed on humic colloids in accordance with the dehydration process illustrated in Figure 4-6 (Kim, 1991).

Humic substances may sorb to mineral surfaces via a number of mechanisms: (i) hydrophobic sorption, (ii) hydrogen bonding, (iii) ligand exchange, (iv) cation exchange, and (v) anion exchange (Thurman, 1985a). Numerous investigations of organic-mineral and organic-metal-mineral complexes have been conducted to establish the partitioning of metals in natural waters (see Thurman, 1985a; Carlsen, 1989; and Stumm, 1992 for listings). Sorption of organic matter on minerals such as $\gamma\text{-Al}_2\text{O}_3$, silica, or iron oxyhydroxides (goethite, hematite) is a function of pH (Krummert and Stumm, 1980). The coating of mineral surfaces with organic matter will thus affect sorption of radionuclides (Bidoglio et al., 1988).

Moulin and Stammose (1988) studied the effects of humic acids on the sorption of Am(III) by colloidal silica. They observed that sorption of the humic acids on silica is inversely related to ionic strength, pH, and humic acid concentration. At constant ionic strength (0.01 M), Am(III) uptake is inversely related to humic acid concentration and pH. At high pH, the humic acids form complexes with Am(III), which remain in solution, whereas, at pH less than 5, the humic acids are sorbed on the mineral surface and thus enhance the sorption of Am(III).

4.4.2 Colloid Stability and Transport

If actinides and other radioelements can sorb onto pseudocolloids or form true colloids, the stability of the particles in suspension is of critical importance in colloid-mediated transport. In the case of pseudocolloids, the availability of natural or human-introduced particles for radionuclide transport in solution is affected through several mechanisms. Particles may be introduced through the precipitation of crystalline and amorphous mineral phases in response to chemical saturation. In a groundwater system, particles may also be released from the aquifer matrix to solution. This release may be due to electrostatic dispersion brought about by changes in solution ionic strength, or due to dissolution of a more soluble matrix to expose and release the colloid. Amorphous phases and colloidal gels may crystallize into more stable, less sorptive phases. Obtaining representative samples is also difficult due to mechanical disruption of primary and secondary minerals owing to shearing and grinding of mineral surfaces induced by hydrodynamic forces or autogrounding between suspended particles. For metal-oxyhydroxides, particle stability is a function of pH, Eh, and the total concentration of the metal (e.g., Fe, Mn, Al, Ti, Si) in solution (Stumm and Morgan, 1981). The presence of other ligands such as HCO_3^- and SO_4^{2-} and $p(\text{CO}_2)$ can also affect the formation of oxides by consuming metal ions in the precipitation of carbonate, sulfate solids. Also, as discussed above, the binding capacity of the particles depends on surface charge, which is determined, in part, by the dissociation of water molecules at the mineral-water interface. For this reason, the sorption of radionuclides on oxides and oxyhydroxides is a function of solution pH. If changes in solution chemistry result in desorption of radioelements, they are free to sorb onto the immobile medium.

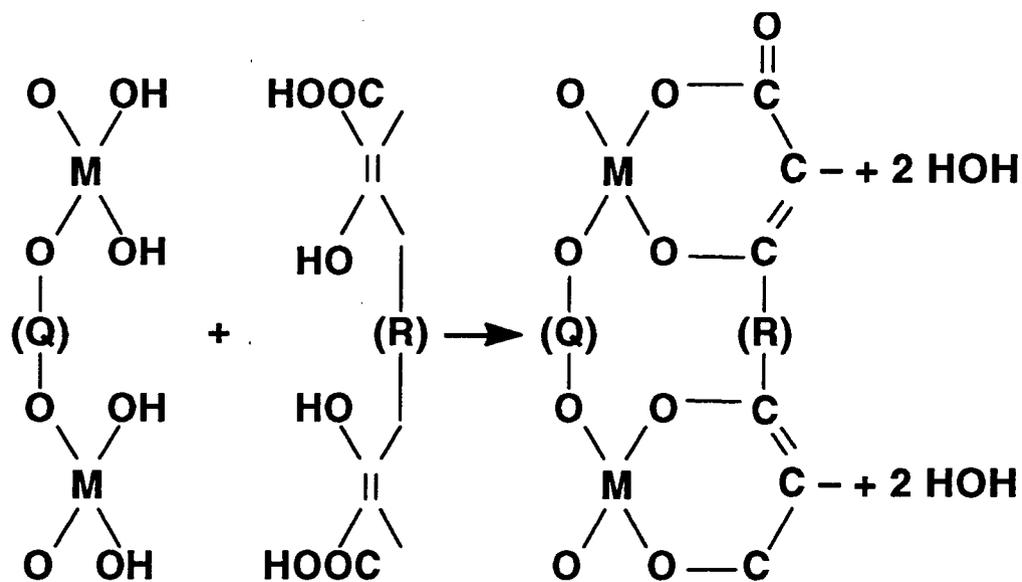


Figure 4-6. Dehydration mechanism for sorption of radiocolloid on humic colloid

In addition to pH controls on the sorptive capacity of colloidal particles, the stability of the colloidal suspension of charged particles varies as a function of pH, ionic strength, and solution chemistry. In the presence of poorly hydrolyzed cations such as Na^+ , the EDL around charged particles extends further into the solution (Hunter, 1987). This phenomenon can cause the expansion of swelling clays, and also tends to promote dispersion of charged particles. In a similar manner, at low ionic strengths or with predominantly monovalent cations, the EDL expands outward from particle surfaces, stabilizing the colloids in solution through electrostatic repulsion. At high ionic strengths, the double layer collapses, and the charged particles begin to flocculate (agglomerate) and come out of suspension due to gravity settling and filtration (Shainberg, 1990).

Variations in overall solution chemistry and moisture content of the medium also influence the magnitude of the ionic strength effect. Degueldre (1993), in colloids from granitic waters in Switzerland, observed that the number of colloidal particles was not affected in a systematic way by increasing Na^+ concentration, but that an order of magnitude increase in Ca^{2+} concentration decreased colloid concentration by four orders of magnitude (Figure 4-7). This observation suggests that the higher charged Ca^{2+} electrolyte more effectively collapsed the EDL and promoted particle agglomeration. Variations in pH also affect particle stability. At low pH, the surface charge is high, and edge-to-plane bonding of clays occurs, as well as bonding of positively charged oxides to negatively charged clay surfaces and organic macromolecules (Ryan and Gschwend, 1990). Under these conditions, clay dispersion is low, flocculation and agglomeration occur, and the suspension is destabilized. As the pH increases towards the pH_{ZPC} , the positive surface charge of the oxides decreases and bonding to clays diminishes. At high pH, oxides exhibit a negative surface charge and actively repel the negatively charged clays, dispersion is enhanced, and the clay colloids are kept in suspension (Suarez et al., 1984).

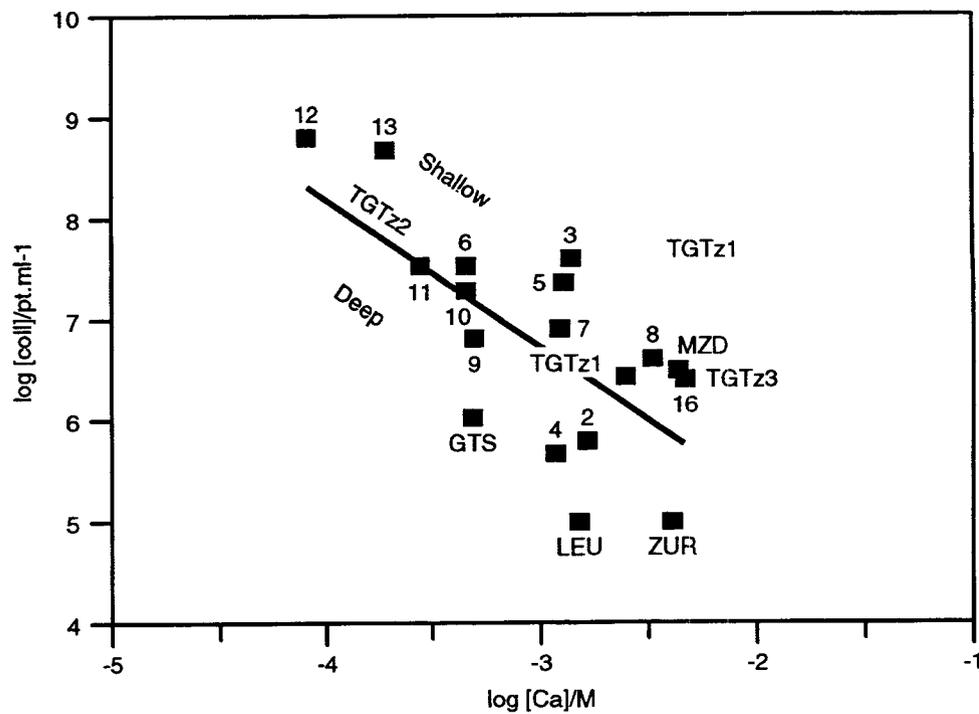
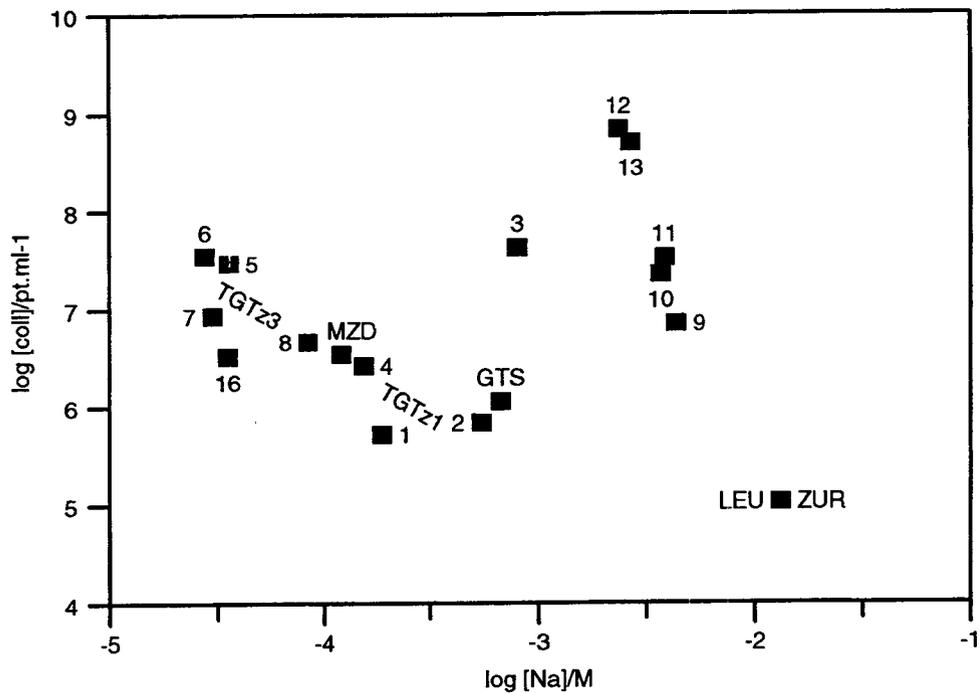


Figure 4-7. For granitic groundwaters collected from Switzerland: (a) colloid concentration (>100 nm) versus Na⁺ concentrations (molarity), (b) colloid concentration (>100 nm) versus Ca²⁺ concentration (molarity). TGT—Transitgas Tunnel (Zones 1, 2, 3), MZD—Menzenschwand, LEU—Leuggern, ZUR—Zurach, GTS—Grimsel Test Site (adapted from Degeldre, 1993)

Wan and Wilson (1994) have developed experimental procedures to examine the role of the air-water interface in particle transport. These experiments have used synthetic glass meshes to simulate different types of pore networks. Work was conducted using a total particle concentration of about 5×10^{16} particles per liter. Synthetic hydrophobic and hydrophilic particles (0.5 to $\sim 1 \mu\text{m}$) were introduced into a low-flow system where flow rate, wettability, particle charge, and ionic strength could be controlled. The background electrolyte was varied from 0.001- to 0.1-M NaNO_3 , and pH was maintained at about 6.6. Flow rates varied from 1.5 to $15 \text{ mL} \cdot \text{h}^{-1}$. In general, due to strong capillary forces, most particles adsorbed at the air-water interface, especially particles that are positively charged. Very few hydrophilic particles adsorbed at the glass-water interface. Increasing hydrophobicity increases particle adsorption at the glass-water interface. Changing ionic strength and flow rate indicate that sorption at the air-water interface is irreversible, while decreasing ionic strength or increased flow rate will lead to desorption at the glass-water interface. Based on the experimental results, the authors suggested that if the air-water interface is static, it may serve to retard radionuclide transport. If the interface is dynamic, however, it may act to enhance colloid transport (Wan and Wilson, 1994).

Column transport experiments (Read et al., 1993) support the migration of Th as a pseudocolloid. Field studies also support the link. Read and Hooker (1989) proposed transport and strain filtering of Th-pseudocolloids with natural Fe-oxides as a mechanism of Th-transport at the Broubster natural analogue site in Scotland. In contrast, uranium was transported as a dissolved species, with minimal colloid formation association. Similar relationships were observed in the Poços de Caldas analog site in Brazil (Miekeley et al., 1991). Vilks and Degueldre (1991) conducted experiments to examine the sorption of ^{85}Sr , ^{131}I , and ^{137}Cs onto natural colloids (40 nm to $1 \mu\text{m}$) collected from the groundwaters at the Grimsel Test Site, Switzerland. The particles were largely organics, spherical silica particles, and aluminosilicates (Degueldre et al., 1989). Cs and Sr strongly sorbed onto the colloids, but ionic strength was only weakly associated with particulate concentration (Vilks and Degueldre; Degueldre et al., 1989). Because of the low concentrations of natural colloids ($1.5 \times 10^{-4} \text{ g} \cdot \text{L}^{-1}$) in the Grimsel system, it was concluded that the risk of colloid-enhanced transport was minor.

4.4.2.1 Organic Colloid Transport

Microbes in soils or unsaturated sediments tend to be located on the surface of minerals because many organic compounds that serve as nutrients for the microorganisms are there (Thurman, 1985a). Bacteria will attach to mineral surfaces with *pili* (filaments) or a mucilage excrement. If the bacteria are active, they will consume the organic matter (forming simpler forms, such as CO_2) while at the same time modifying the mineral surface. Attachment of viruses to hydrological substrates has been observed to be a function of groundwater pH, ionic strength of the groundwater, and the fraction of organic carbon of the soil (Kinoshita et al., 1993).

Bales et al. (1989) studied the transport of viruses through a core of tuff from the NTS. Although the pores of the tuff were larger than $0.1 \mu\text{m}$ and the viruses were only $0.023 \mu\text{m}$ in diameter, the viruses were largely excluded from the porous matrix of the tuff. They were, however, retarded relative to calculated residence time for fracture transport of soluble species alone. Bales and others proposed that the observed retardation was due to migration of the microorganisms into dead-end pores of the tuff, where they were retained. Kinoshita et al. (1993) noted that retention of viruses in sandy soils is relatively insensitive to pH over the range of 5.7–8.0. Retention is reversible but slow for hydrophobic species. These investigators used a colloid-filtration model to evaluate the movement of viruses through

soil columns. The model predicts that hydrophilic viruses should move through soils with little retardation.

Humic substances adsorbed to colloidal mineral surfaces will affect not only the sorption properties for radionuclide species, but also the transport properties of the groundwater colloids by changing the coagulation and subsequent flocculation of colloidal material. In small amounts, humic substances and dissolved salts can sorb to the mineral surface, bridging the repulsive barrier between particles (van Olphen, 1987). At higher concentrations of organic matter, mineral particles become coated with organic matter and are stabilized in suspension because of repulsion between organic molecule functional groups (Figure 4-8) (Liang and Morgan, 1990). Humic substances are coiled long-chain molecules that may exhibit cross-linking among functional groups. Most of the electrical charge of the humic substance is associated with dissociation of the COOH groups (Cornel et al., 1986). Thus, at high pH, there will be more dissociation and less interaction of the coils because of electrostatic repulsion. The shape is more spherical for those humic substances with molecular weight (MW) < 2600. At low ionic strength, the colloids are fully extended but shrink with increasing ionic strength. This property of changing geometry will have an effect on the transport properties of humic substances.

Several studies have been conducted to model the transport of organic matter in groundwater systems (Harvey and Garabedian, 1991; Williams et al., 1993). Organic molecules may be modeled as rigid impenetrable spheres or as large flat surfaces. The form will affect the transport properties.

The formation and transport of radionuclide-bearing organic colloidal material is considered an important aspect of the performance of a HLW repository. Knowledge of the composition and abundance of naturally occurring organics and microbes, as well as those introduced by human activity, is, therefore, essential for establishing a baseline for organic chemistry effects in the near and far fields. The extent of pseudocolloid formation, binding of radionuclides by microorganisms, and enhanced solubility will be a function of aqueous chemistry. The transport properties, in turn, will be a function of groundwater chemistry and the nature of organic matter present. However, the importance of organic and microbial materials is difficult to predict at this time because of the dependence on coupled systems such as groundwater flow and aqueous geochemistry.

4.5 POTENTIAL INFLUENCE OF YUCCA MOUNTAIN SETTING AND ENVIRONMENT ON SORPTION, TRANSPORT AND FILTRATION OF COLLOIDS

Natural colloids have been observed in the saturated groundwaters of the Yucca Mountain vicinity. These natural colloids include both inorganic and organic colloids. Many of these materials reflect the host rock mineralogy. Laboratory and field studies from other sites have shown that these materials can sorb radioelements that will be important in the inventory of a HLW geologic repository. In addition, several of the actinides are known to form colloidal particles through hydrolysis and polymerization under laboratory conditions, although it is unclear if this formation will be significant under the groundwater conditions in the repository environment. Generally, however, colloid concentrations seem to be fairly low, although techniques for sampling colloids in the field still suggest that there is an uncertainty in the amounts of colloids at Yucca Mountain. For example, concentrations from springs and wells in the vicinity (Kingston and Whitbeck, 1991) are typically higher than those reported for J-13 well water (Kerrisk, 1987).

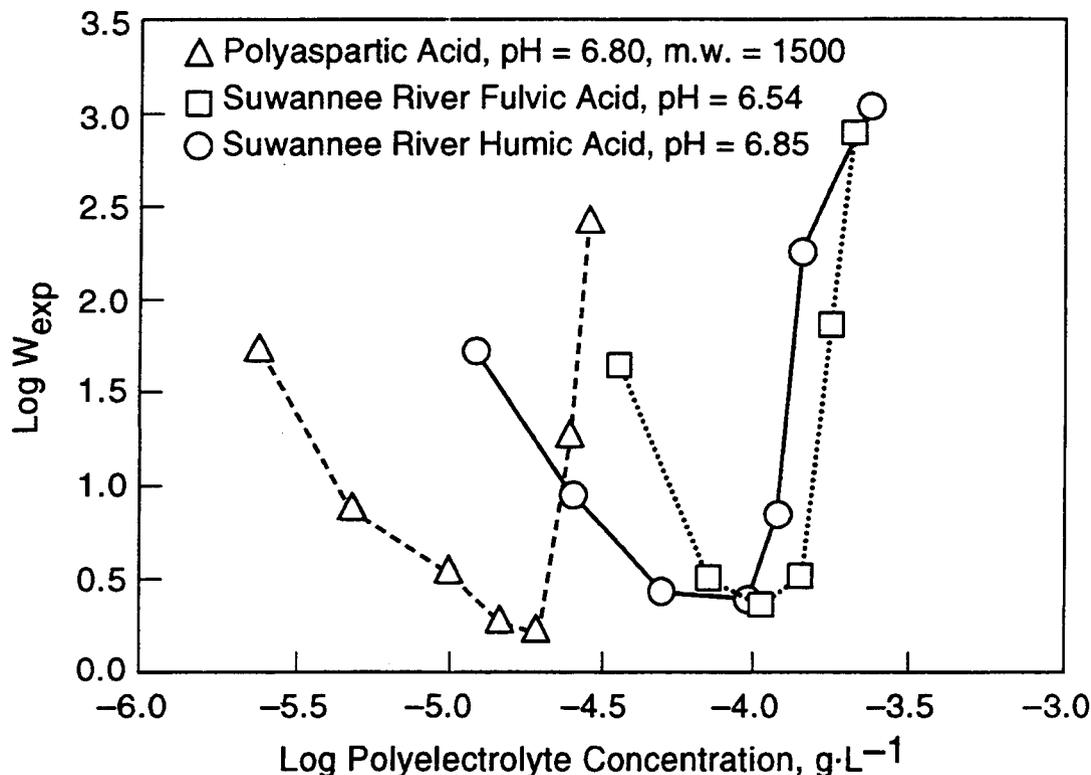


Figure 4-8. Experimentally derived stability ratio, W_{exp} , of a hematite suspension, plotted as a function of polyelectrolyte concentration in the presence of 1 millimolar NaCl. Hematite concentration is $17.2 \text{ mg} \cdot \text{L}^{-1}$ (adapted from Liang and Morgan, 1990)

The degree to which colloids in the saturated waters reflect the conditions in the unsaturated zone remains uncertain. Transport of colloids under unsaturated conditions is poorly understood, and only recently have laboratory methods been developed to address these issues (Wan and Wilson, 1994). Preliminary porosimetry data at Yucca Mountain suggest that matrix transport of colloids will be limited, but that fracture apertures are large enough to allow colloid transport by fracture flow. In addition, laboratory studies indicate that the sorption of radionuclides to form pseudocolloids is strongly dependent on system chemistry. Field studies from other areas also indicate that the solution chemistry has an effect on the number of colloid particles in suspension. Some geochemical models exist to take into account some of this dependence, but PA models have generally focused on empirical approaches.

Although natural colloids are present in the Yucca Mountain environment, the extent to which they could contribute to overall radionuclide transport remains unclear. If the number of colloids in the unsaturated (and saturated zone) is small, then the contribution is likely to be minimal. However, until the effects of system chemistry on colloid stability and radionuclide sorption are explicitly considered, there will continue to be uncertainty about the role of colloids in performance assessment.

5 MODELING COLLOID-MEDIATED TRANSPORT OF RADIONUCLIDES

This section provides a review of the colloid transport phenomena relevant to radionuclide migration at a HLW repository site. The KTUs discussed in Section 1.2.1 identify several technical concerns pertinent to the transport of colloids under partially saturated conditions. These concerns can be consolidated into a single fundamental topic: the ability to simulate the coupled transport of soluble species and colloids in a partially saturated and fractured porous medium. Various governing equations and mathematical formulations for the transport of colloids are provided and discussed. Limitations of existing models regarding colloid transport under the aforementioned conditions are identified and discussed. Based on the review, a recommendation on a systematic approach to assessing the possible contribution of colloids to radionuclide release and transport at a HLW repository site is discussed. The mathematical equations presented in this section are not intended to address every potential phenomenon that can affect the transport of colloids at a HLW disposal site. Rather, these equations are discussed to provide a conceptual framework for how colloidal particle transport can be analyzed.

5.1 COLLOID TRANSPORT MODELING

Investigation of colloid transport at HLW disposal sites has been going on for over a decade. Some examples are Avogadro et al. (1981), Avogadro and Lanza (1982), Avogadro and de Marsily (1984), Champ et al. (1982), Eichholz et al. (1982), Neretnieks (1978), Olofsson et al. (1982a, b), Bales et al. (1989), Castaing (1991), Hwang et al. (1990), Light et al. (1989), Nuttall et al. (1991), and van der Lee et al. (1993). In the early 1980s, the HLW program funded by the NRC at the Sandia National Laboratories examined the importance of colloid transport from a PA point of view (Bonano et al., 1984; Nuttall et al., 1984; Bonano and Siegel, 1984; and Bonano and Beyeler, 1985, 1987). The first three publications provide a review of the literature and issues of colloid transport in PA of HLW, whereas the latter two present very simple models of colloid transport in a single fracture and results obtained with those models using parameter values obtained primarily from the filtration literature. These models, however, have been applied only under fully saturated conditions. Despite these and other studies related to colloids, a model for colloid transport adequate for use in PA is still lacking, even for saturated conditions. The lack of such a model can be attributed to three reasons: (i) lack of data relevant to colloid transport at a HLW disposal site, (ii) poor understanding of complex phenomena governing colloid transport and capture at a HLW disposal site, and (iii) inability to translate detailed mechanistic models into PA models. For these reasons, it has not been possible to assess the relative importance of colloid transport, in contrast to the transport of dissolved species, in the PA of a HLW repository.

5.2 PHYSICAL PROPERTIES OF COLLOIDS

Colloids exhibit physical properties and characteristics that set them apart from soluble species. These properties are important in determining both the fate of the colloids (i.e., their rate of transport and the attachment to or detachment from the walls of the channel through which they travel) and their ability, in the case of pseudocolloids, to adsorb soluble radionuclides. Some of these properties include: rheology; instability of colloidal suspensions (segregation, flocculation or aggregation, and disproportionation, among others); surface charges; and the shape, size, and size distributions of colloids.

5.2.1 Rheological Properties

The viscous behavior of dilute colloidal suspensions generally exhibits approximately the same viscosity as the dispersion medium, and the suspension behaves as a Newtonian fluid. At a higher concentration, the solutions remain Newtonian, with the viscosity increasing in proportion to the volume fraction of the dispersed phase. At low volume fractions, ($\phi < 0.02$), the viscosity of colloidal suspensions is given by Einstein's equation:

$$\mu = \mu_0(1 + k\phi) \quad (5-1)$$

where

- μ_0 = viscosity of the suspending medium
- μ = viscosity of the colloidal suspension
- ϕ = volume fraction of the dispersed phase
- k = an empirical shape factor equal to 2.5 for spheres

For higher concentrations, particularly of asymmetrical or flocculated particles, the behavior of the suspension may become non-Newtonian. In this case, the viscosity is a nonlinear function of ϕ , and Eq. (5-1) is no longer valid.

5.2.2 Inherent Instability

An important distinction between colloid suspension and solutions is stability. The stability of a colloidal suspension is an important property for it will, to a large extent, determine the ability of colloids to remain in suspension. If colloids are removed from suspension, then they cannot be transported. Processes that influence the stability of colloidal suspensions include: (i) phase segregation, (ii) aggregation or flocculation, and (iii) size disproportionation.

5.2.2.1 Phase Segregation

Colloidal suspensions may be unstable with respect to the spatial distribution of the colloids because the density of the latter is usually quite different from that of the suspending medium. The ratio of the density of colloids to the density of the suspending medium can be greater than 8 to 10 relative to water at 25 °C, whereas for emulsions of oil and water, the ratio is considerably smaller (e.g., <1 to 2). In a gravitational field, the colloids will tend to settle to the bottom of the container (sedimentation) if they are denser than the suspending medium, or rise toward the top (creaming) if they are lighter. Typical rates for sedimentation of colloids from geologic media in a static aqueous solution, as a function of size, are shown in Table 5-1. The results in this table indicate that the sedimentation rate, or settling velocity, of colloids is a strong function of size. Mathematically, this effect will be shown in Section 5.5.

5.2.2.2 Flocculation or Aggregation

The flocculation or aggregation phenomenon can be described as clumping or sticking together of dispersed colloids. The flocs or aggregates may be adherent or remain loosely attached, depending upon the interactive forces (attractive or repulsive) between colloids. The process can be explained

Table 5-1. Typical sedimentation rates as a function of colloid size^a

R, μm	Velocity
100	130 $\text{cm} \cdot \text{min}^{-1}$
10	1.3 $\text{cm} \cdot \text{min}^{-1}$
1	0.013 $\text{cm} \cdot \text{min}^{-1}$
0.1	0.19 $\text{cm} \cdot \text{d}^{-1}$
0.01	0.70 $\text{cm} \cdot \text{yr}^{-1}$
^a Berg, J. 1992. <i>Surface and Colloid Science</i> . Summer Short Course. Seattle, WA: University of Washington.	

phenomenologically on the basis of attraction and repulsion forces between two (or more) colloids. When two colloids are sufficiently close, there are large attractive forces between them known as the London-van der Waals forces arising from molecular oscillations and electric fields. These forces represent an intermolecular potential energy called configurational energy, that decreases rapidly as the intermolecular separation distance increases. As the colloids get even closer, their electron clouds start to overlap, leading to increased repulsive forces. At a certain separation, a minimum in potential energy occurs; this point represents a low point in free energy of the two (or more) colloids. The stability of the colloidal suspension is dependent on which of these two forces, repulsive or attractive, dominates.

5.2.2.3 Particle Size Disproportionation

Particle size disproportionation refers to the process whereby large particles grow at the expense of smaller ones. The process consists of molecules or ions from smaller particles dissolving into the medium, while at the same time dissolved molecules incorporate themselves into the larger particles. This process can occur when the solubility of the material from the smaller particles is greater than that of the material from the larger particles, due to the Kelvin effect. If the particles are only sparingly soluble in the dispersion medium, the process of disproportionation will be slow. However, given the regulatory period of interest (10,000 yr following closure of the repository), this process may need to be considered in predicting the behavior of colloidal suspensions. The occurrence of this process could have significant consequences on the behavior of colloid systems.

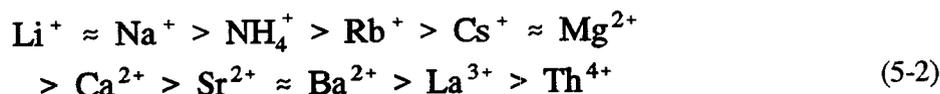
5.2.3 Colloids Surface Charge

Colloids can have positively or negatively charged surfaces. Since ionizable functional groups such as hydroxyl (O-H) groups are often present at the surface of a particle, and the solution pH determines the ionization state of a group, the particle charge is controlled by the pH of the system.

At low pH values (<2 to 3), silica surfaces carry positive charges, while at high pH values the surfaces are negatively charged. In addition to protons, metals and anions, such as phosphate and carbonate, may form complexes on colloid surfaces and change the net surface charge. When such reactions occur, the pH at which the surface charge is neutral is called the zero point of charge (ZPC). Clays and some organic pollutants are negatively charged in neutral pH waters (~7); whereas, ferric hydroxide and some other metal hydroxides have a positive surface charge (van Olphen, 1977). Surface charge may also be caused by isomorphic replacements that occur during crystallization. These isomorphic replacements are pH independent. Atomic substitution in the crystalline lattice of similar size atoms with different valences disrupts the electroneutrality of the lattice. For example, Mg atom replacement of an Al atom in a kaolinite crystal lattice creates a negative charge on the crystal surface.

Although less common, the reverse can also occur whereby a positive charge is created (Bohn et al., 1985).

Two opposing forces operate on ions in solution at the particle-solution phase boundary. Ions are attracted to the electrostatic surface charge of the opposite sign, and they are repelled from the surface due to the induced ion concentration gradients toward the surface (charge of the same sign). The concentration of positively charged particles is greatest near the negative particle-solution interface and decreases away from the interface. However, this concentration does not account for selective cation adsorption. Higher valence cations bind more strongly than lower valence cations. A cation with a smaller dehydrated radius will possess a greater charge density that will attract a larger hydration sphere and decrease the strength of adsorption. Therefore, relative adsorption potential can be represented by a lyotropic series. For example, for montmorillonite, it can be expressed as (Bohn et al., 1985):



← Ease of Replacement

Among the ions shown in the above expression, Rb^+ has a smaller dehydrated radius than Cs^+ , and, as a result, the former is more readily displaced from a colloid surface than the latter. The process of selective displacement or removal of adsorbed ions from colloids would be important for transport of radionuclides in a geologic repository with changing characteristics over the large distances of interest (i.e., kilometers).

5.2.4 Morphology of Colloidal Dispersions

Colloids in groundwaters can be found in a wide variety of shapes and sizes requiring statistical techniques to characterize them. Such characterization of colloidal systems is necessary because, as is shown mathematically in Section 5.5, they strongly influence the susceptibility of colloids to settling and filtration, adsorption, and transport.

Colloids can have a variety of different shapes. Solid soil particles that have some measurable solubility also tend toward the spherical shape by the same mechanism as that of particle-size disproportionation. However, over short times, the particles may retain nonspherical shapes due to the slow disproportionation process. A schematic of common shapes of aqueous colloids is provided in Figure 5-1. For mathematical treatment, colloids are often considered spherical for most colloid transport analyses. The main reason for the assumption is the difficulty in modeling nonspherical particles. It is customary to simulate nonspherical particles as spheres of an equivalent diameter. A number of colloid properties, some of which have been alluded to earlier in this section, depend on colloid shape, size, density, and distribution. These characteristics may have considerable influence on the migration and transport of colloids in a geologic environment.

Most colloidal suspensions have a range of particle sizes, and are therefore referred to as *polydisperse* suspensions. Single-size colloids are termed as *monodisperse* suspensions. Polydisperse colloidal suspensions can be characterized as to size and shape of the colloids in terms of a few parameters as described as follows.

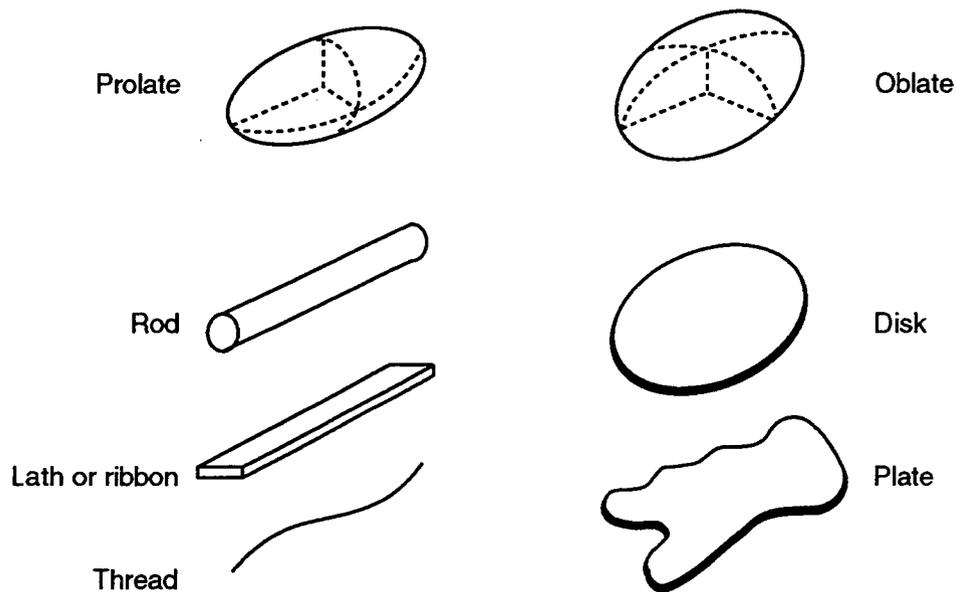


Figure 5-1. Schematic representation of nonspherical colloid particles

The mean colloid diameter, \bar{d}

$$\bar{d} = \frac{\sum n_i d_i}{\sum n_i} = \sum f_i d_i \quad (5-3)$$

where

- n_i = number of colloids with diameter d_i
- d_i = diameter of colloids of i^{th} size

This mean diameter is most frequently used to describe a distribution. The mean diameter alone, however, does not indicate the width of the distribution of colloid diameters; this measure is described by the variance, σ^2

$$\sigma^2 = \frac{\sum n_i (d_i - \bar{d})^2}{\sum n_i} \quad (5-4)$$

or its positive square root, the standard deviation, σ . It is noted that the larger the σ , the wider the size distribution. Another higher moment is often used to characterize colloid distributions further.

The third moment about the mean, which is called the skewness, m_3

$$m_3 = \frac{\sum n_i (d_i - \bar{d})^3}{\sum n_i} \quad (5-5)$$

The skewness shows the asymmetry of the distribution. A positive value of m_3 denotes a long tail of the distribution toward larger-diameter colloids.

5.3 COLLOID FILTRATION PHENOMENA

The effectiveness of colloids in enhancing (or retarding) radionuclide migration is dependent on the efficiency with which these particles are transported through the groundwater system. Colloid migration may be enhanced relative to fluid flow due to volume exclusion, hydrodynamic chromatography effects, and reduced particle/medium interaction (Grindrod, 1991). Conversely, colloids may be retarded through various physical and chemical filtration mechanisms resulting from interaction between the different phases of the colloid-rock-water system. McDowell-Boyer et al. (1986) divided filtration processes into three basic classes: (i) surface (cake) filtration, (ii) straining, and (iii) physical-chemical filtration (Figure 5-2). The following subsections briefly summarize these different mechanisms.

5.3.1 Surface (Cake) Filtration

Surface filtration involves the buildup of a barrier at the water-pore interface (Figure 5-2). This type of filtration occurs when the particles are too large to enter the pores of the medium. As the particles are stopped at the surface, they are held in place by the fluid flow, and a mat or cake of particles is gradually formed. With time, the filter cake thickens, and its porosity and permeability decrease through compression. Fluid flow through the mat decreases, and there is a pressure drop across the cake. Filter cake permeability is also a function of particle aggregation. Destabilized colloidal suspensions (e.g., low ionic strength, monovalent cations) tend to form a more porous arrangement than those cakes formed from stable suspensions (McDowell-Boyer et al., 1986). The surface (cake) filtration may be of less relevance at the Yucca Mountain site in view of the fact that transport of colloids may occur primarily through fractures.

5.3.2 Straining

If the particles are small enough to enter the porous medium, the tortuous path they must follow may eventually lead to a constriction that is too small for them to pass (Figure 5-2). This constriction leads to a straining of the colloids from solution. Laboratory tests using plastic beads in a mineral oil suspension to minimize particle-medium interaction (Sakthivadivel, 1969) determined an empirical measurement of the effectiveness of filtration by straining based on the media pore diameter (d_m) and the particle diameter (d_p). For ratios of $d_m/d_p < 10$, particles are effectively denied entry into the porous medium (surface filtration), while for $d_m/d_p > 20$, the particles are small enough to pass through the medium relatively unimpeded. For the intermediate range of $10 < d_m/d_p < 20$, straining is most effective, filtering particles from suspension. In an attempt to consider a population of suspended particles with variable diameter, Sherard et al. (1984) observed that fine particles would not enter a porous media for

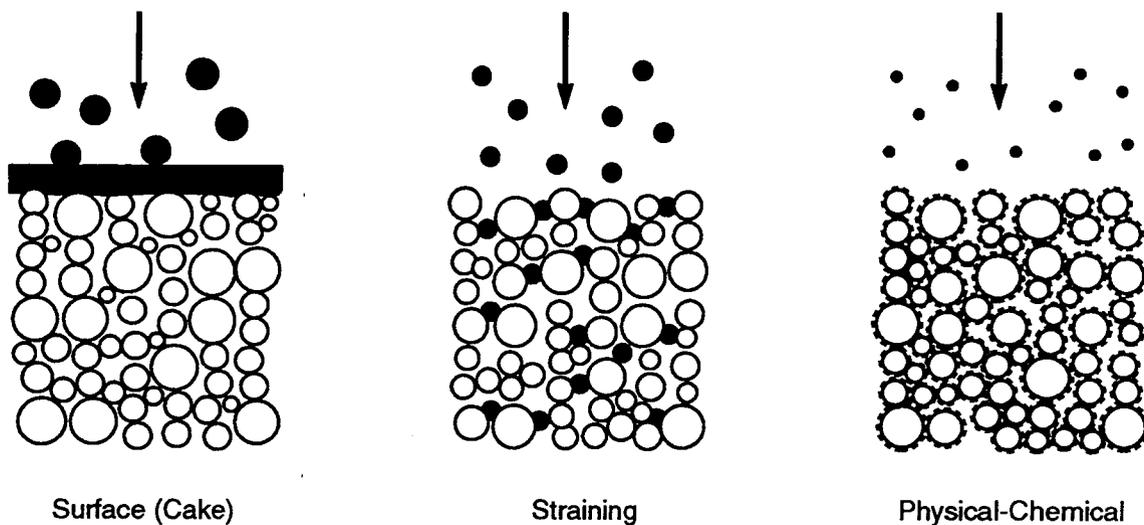


Figure 5-2. Mechanisms for colloid straining in porous media (adapted from McDowell-Boyer et al., 1986)

the value of $d_{m,15}/d_{p,85} < 9$. In this relation, $d_{m,15}$ is the pore diameter that exceeds the pore diameter of 15 percent by weight of the coarse media, and $d_{p,85}$ is the upper diameter limit for 85 percent of the suspended particles by weight. Assuming a typical pore diameter of 100 nm in the Yucca Mountain tuffs, based on mercury porosimetry measurements (Daniels et al., 1982), particles greater than about 5 to 10 nm would be effectively removed from suspension by straining during transport through the rock matrix.

5.3.3 Physical-Chemical Filtration

Particles may be removed from suspension by interaction with the pore walls, either through physical processes such as Brownian diffusion and gravitational sedimentation or through chemical processes such as sorption due to electrostatic attraction (Figure 5-2). According to McDowell-Boyer et al. (1986), colloidal particles are dominantly transported by Brownian diffusion to a collector surface. Brownian motion can keep small particles in suspension by countering settling due to gravitational force. Brownian diffusion can retard colloid transport through contact with the medium, longer trajectories, or diffusion into constricted or dead-end pores (de Marsily, 1986). Herzig et al. (1970) note that Brownian diffusion is generally negligible for particles $> 1 \mu\text{m}$ diameter.

Electrochemical forces can either repel or attract particles to the geologic medium. As discussed previously, minerals that make up the geologic media have surface potentials due to lattice substitution and disassociation of surface hydroxyl groups. These groups can attract and repel charged particles with

a surface potential, including pseudocolloids and true colloids resulting from hydrolysis and polymerization. The diffuse EDL represents the distance the charge of the particle or medium extends away from the solid-water interface. McDowell-Boyer et al. (1986) noted that calculations based on double-layer theory alone underpredict observed colloid attachment, suggesting that other forces need to be considered. London-van der Waals attractive forces also contribute to the attachment of suspended particles to a substrate (McDowell-Boyer et al., 1986; McDowell-Boyer, 1989). Herzig et al. (1970) noted that for particles larger than about 100 nm in diameter, these attractive forces will tend to exceed random-movement energy, but for smaller particles, the reverse is true. Net interaction (joules) versus particle-medium separation distance at a variety of ionic strengths is shown in Figure 5-3. As a particle approaches the medium (or collector), the separation distance decreases. At distances on the order of 100 nm or less, the particle begins to be affected by the electrostatic repulsive forces. If the particle has enough energy (imparted by hydrodynamic forces, thermal energy, Brownian diffusion, etc.) to overcome this energy barrier, it can approach closer and reaches the primary minimum due to attractive forces at separation distances on the order of 0.5 nm. The thickness of the EDL decreases with increasing ionic strength, as discussed above. This decreasing thickness of the EDL suggests that the net interaction also will vary as a function of ionic strength. At low ionic strength, the electrostatic repulsion force dominates the attractive forces, and the energy barrier to particle attachment becomes larger. The magnitude of the electrostatic repulsion force also depends on the magnitude of the surface charges of both the colloids and the collector (the geologic medium, in this case) (see Section 5.5). As the ionic strength increases, the EDL is compressed, and the energy barriers to particle attachment decrease until at ionic strengths on the order of 0.5 M or greater, attachment is favored at all separation distances. The primary energy minimum (or attractive energy well) is finite because of Born repulsion operating at short distances. McDowell-Boyer (1989) suggests that although Born repulsion has no effect on the height of the energy barrier, the energy well would have no lower limit if it were neglected.

After particles have been deposited, there is the possibility that they may be resuspended. The distances calculated for the energy attachment well (0.3 to 1 nm) are generally smaller than the diameter of the particle. While London-van der Waals forces generally predominate at these ranges, energy provided from Born repulsive forces, or thermal and hydrodynamic energy, can overcome the attraction energy well and lead to particle erosion and re-entrainment (McDowell-Boyer, 1989). The magnitude of the force necessary to dislodge and resuspend attached particles will also vary as the system chemistry changes. An additional possibility is that a decrease in the solution ionic strength may extend the EDL, leading to particle release (Kallay et al., 1987). Kallay et al. (1987) also indicate that sweeping the resuspended particle away from the surface is necessary to prevent reattachment.

Although the size of colloids makes them vulnerable to several different filtration mechanisms, it is also possible that particle size (Olofsson et al., 1985; Pigford, 1989; Bales et al., 1989) will lead to volume exclusion and a less tortuous, more rapid path to the accessible environment. In pores and fractures, the water velocity distribution is such that the maximum velocity is along the centerline of the fracture, while minimum velocity occurs at the fracture wall. Because of their size and possibly electrostatic repulsion, colloids most likely will not experience the minimum water velocity, and, consequently, the average colloid velocity may be greater than that of the water. In general, this effect, called hydrodynamic chromatography (de Marsily, 1986), becomes more pronounced with increasing particle diameter. In addition, electrostatic repulsion associated with charged particles will tend to keep the particles away from the walls, further enhancing the effect. Since the particle charge is a function of pH and ionic strength as discussed previously, hydrodynamic chromatography in a natural environment will also vary as a function of solution chemistry (de Marsily, 1986).

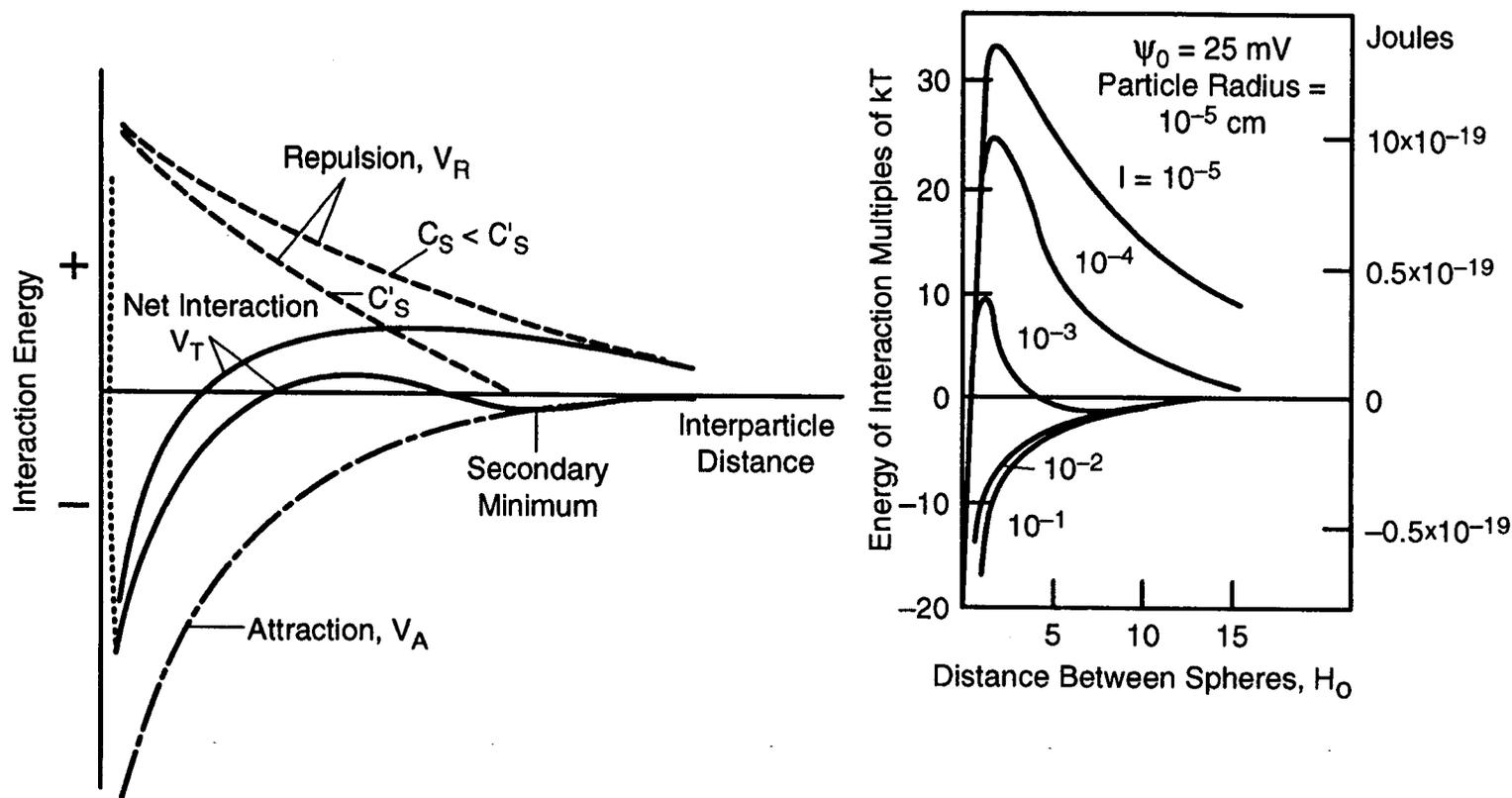


Figure 5-3. (a) Schematic curves showing the interaction energies between two charged particles: V_R = electrostatic repulsion, V_A = van der Waals Attraction, V_T = total net attraction, C_s = electrolyte concentration, C'_s = critical electrolyte concentration to allow coagulation; (b) net interaction energies for constant potential spheres in solutions of different ionic strengths (I): Ψ_0 = electrostatic potential (adapted from Stumm and Morgan, 1981)

5.4 MATHEMATICAL TREATMENT OF COLLOID TRANSPORT

Colloids can interact among themselves and with the walls of the channel bounding the flow and be captured, released, or filtrated out through a variety of phenomena (Bonano et al., 1984; Sharma and Yortsos, 1987) such as: (i) electrostatic forces, (ii) Hamaker or dispersion forces, (iii) Born repulsion, (iv) Brownian motion, (v) hydrodynamic and gravitational forces, and (vi) mechanical stresses. The magnitude with which these different forces act on the colloids and affect their transport depends on a wide range of parameters and properties of the solid bounding the flow, the fluid in which the colloids are suspended, and the colloids themselves, as has been discussed earlier in this report.

It is well documented in the literature that colloid transport in a closed conduit, such as a parallel-plate channel or a capillary tube, is affected by hydrodynamic chromatography effects. In such conduits, at very low Reynolds numbers (creeping flow regime) so that inertial effects are negligible, the velocity profile of the flowing medium is parabolic (Poiseuille flow). For example, van der Lee et al. (1993) conceptually describe the transport of colloids down a parallel-plate channel to consist of two regions (see Figure 5-4). In Region I, at a distance δ away from the walls of the channel, the colloids are not affected by colloid-wall interactive forces and are, therefore, available for transport in the flowing fluid by convection. In Region II ($0 \leq z \leq \delta$), these forces dominate and the colloids are not readily available for transport. As colloids in Region II are removed from the suspension, due to the aforementioned forces, colloids in Region I remain suspended in the flowing fluid. If one calculates the average velocity of the colloid front, fluid velocities in Region II are not included in the calculation because they do not contribute to colloid transport. In contrast, the calculation of the average fluid velocity includes all velocities across the entire width of the channel. Thus, the calculated average velocity of the colloid front can be higher than the average flow velocity of the fluid. Hence, the reason for stating that the colloid-transport mechanism can reduce the average travel time of radionuclides as compared to their migration as dissolved species. Bonano and Beyeler (1987) show how the average velocity of a colloid front can be estimated from the solution of the colloid transport equation, and some of their results are presented later in this section.

5.4.1 Flocculation or Aggregation of Colloids

Flocculation, a phenomenon by which particles agglomerate to form larger ones, plays a significant role in colloid settling out of suspension. The gravitational force acting on colloids is a very strong function of particle size and is responsible for colloid settling (called sedimentation) as shown by the data in Table 5-1. The larger the colloids, the more susceptible these are to gravitational settling; subsequently, they will not be available for transport. Conversely, when colloids do not flocculate they tend to remain in suspension, which facilitates their transport. Kruyt and van Klooster (1930) postulated that the rate of flocculation and, hence, the stability of a suspension, depends on two factors: (i) likelihood or probability of a collision between two or more particles, and (ii) likelihood or probability that the collision will be successful and result in adhesion. The probability of collision is a function of the concentration of the colloids and temperature of the suspension; the higher the values of these variables, the higher the probability of collision. However, a successful collision is also dependent on the electrokinetic force between two or more colloids as described in Section 5.2.

Davis and Yates (1976) used Smoluchowski's theory to develop a flocculation rate for use in the solution of the convective-diffusion of aerosols and hydrosols being transported in a laminar flow in a tube that can be applied to estimate the rate of flocculation of colloids. They developed an expression

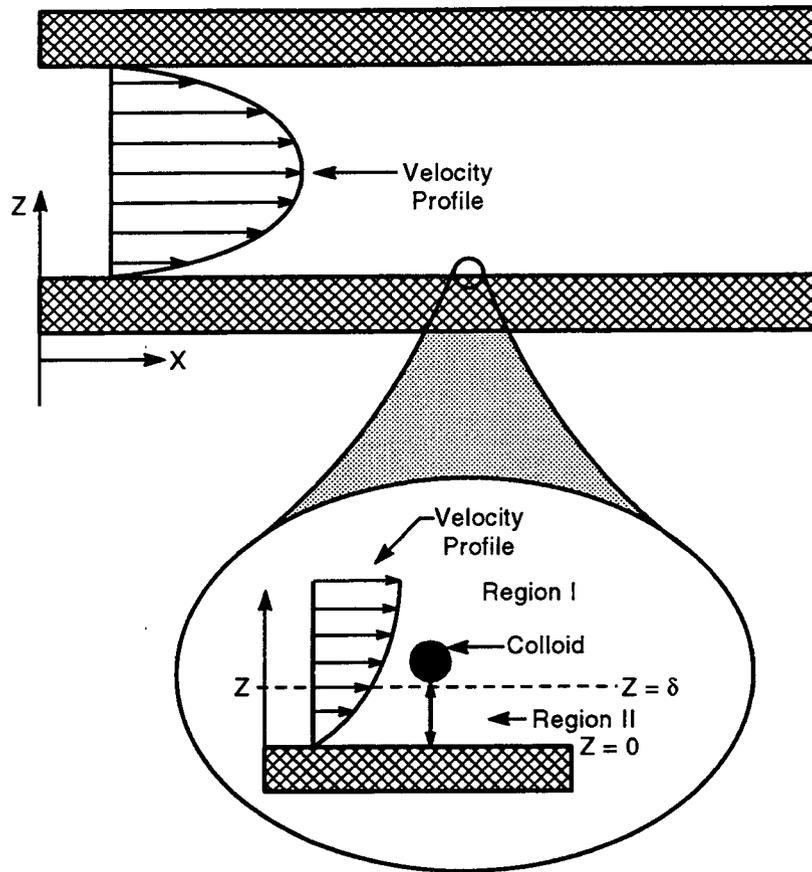


Figure 5-4. Schematic representation of convection (Region I) and attachment (Region II) regions that influence determination of average colloid-front velocity (adapted from van der Lee et al., 1993)

for the net removal of particles of the i^{th} species (i.e., spherical particles of radius, a_i , and mass, m_i) from suspension; the expression is as follows:

$$\phi_i = \frac{1}{2} \sum_{j=1}^{i-1} K_{i-j,j} N_{i-j} N_j - N_i \sum_{j=1}^{\infty} K_{i,j} N_j \quad (5-6)$$

where

- ϕ_i = rate of removal of colloids of the i^{th} species per unit volume due to coagulation
- N_i = number concentration of colloids of the i^{th} species
- $K_{i,j}$ = rate of flocculation of colloids of the i^{th} and j^{th} species

Expressions for the flocculation rate are available in the literature; for example, Bensley and Hunter (1983) have given mathematical expressions for the coagulation rate as a function of the surface potential due to electrokinetic and London-van der Waals forces and other parameters, such as temperature.

5.4.2 External Forces

A variety of external forces act on colloids, and those forces will dominate the interactions between the colloids, the channel through which the latter are being transported, and the carrier or suspending medium in which they are transported. The mathematical representations for these forces are provided in this section for colloids traveling in a parallel-plate channel configuration.

5.4.2.1 Gravitational (Settling or Sedimentation) Forces

Colloids can settle out of suspension due to gravitational forces caused by the difference in density between the colloids and the suspending fluid. For flow in a horizontal channel, the gravitational force can be written mathematically as

$$F_G = -\frac{4}{3}\pi a^3(\rho_c - \rho_f)g \quad (5-7)$$

where

- a = radius of colloid
- ρ_c, ρ_f = density of the colloid and fluid, respectively
- g = gravitational acceleration

5.4.2.2 Electrostatic Forces

As discussed earlier, electrostatic forces can stabilize a colloidal suspension through repulsion, or lead to settling through particle attraction. The electrostatic force acting on a colloid is a function of the colloid's distance from each of the walls in the channel. For a parallel-plate channel, this function can be expressed mathematically as (Bonano and Siegel, 1984):

$$F_E = \frac{\epsilon_d \tau (\phi_c^2 + \phi_w^2)}{2} \left[\frac{g(H, \tau)}{f_z(H)} - \frac{g(H_u - H, \tau)}{f_z(H_u - H)} \right] \quad (5-8)$$

where

- ϵ_d = $4\pi\epsilon_0\epsilon_D$
- ϵ_0 = permittivity of a vacuum
- ϵ_D = dielectric constant of the suspending fluid
- ϕ_c, ϕ_w = surface charge of the colloid and the walls of the channel, respectively

τ = $a\kappa$
 κ = reciprocal of the EDL thickness, which is given as

$$\kappa = \left[\frac{4\pi e^2}{\epsilon_d kT} \sum_{j=1} c_j Z_j^2 \right]^{\frac{1}{2}} \quad (5-9)$$

where

e = electron charge
 c_j = concentration of the j^{th} ionic species
 Z_j = corresponding valence; all other variables have been previously defined
 k = Boltzmann's constant

Equation (5-8) contains two functions, $g(H, \tau)$ and $f_z(H)$, that represent the strength and sign of the electrostatic force and the hydrodynamic resistance force preventing the attachment of a colloid to the walls of the channel. The function $g(H, \tau)$ is given by (Bonano et al., 1984):

$$g(H, \tau) = \left[\frac{2\phi_c \phi_w}{(\phi_c^2 + \phi_w^2)} - e^{-\tau H} \right] \frac{e^{-\tau H}}{1 - e^{-2\tau H}} \quad (5-10)$$

and $f_z(H)$ has been tabulated by Payatakes et al. (1974). It should be noted that transport of a colloid in a closed parallel-plate channel is affected, in principle, by the presence of both the bottom and top walls. Therefore, Eq. (5-8) includes the effects of colloid interactions with both walls, with H and H_u being the dimensionless separation of a colloid of radius a from the bottom and top wall, respectively, and given as

$$H = \frac{b}{a} + \frac{z}{a} - 1 \quad (5-11)$$

and

$$H_u = \frac{b}{a} - \frac{z}{a} - 1 \quad (5-12)$$

where

b = half-width aperture of the channel
 z = is the position from the bottom wall of the channel (see Figure 5-5)

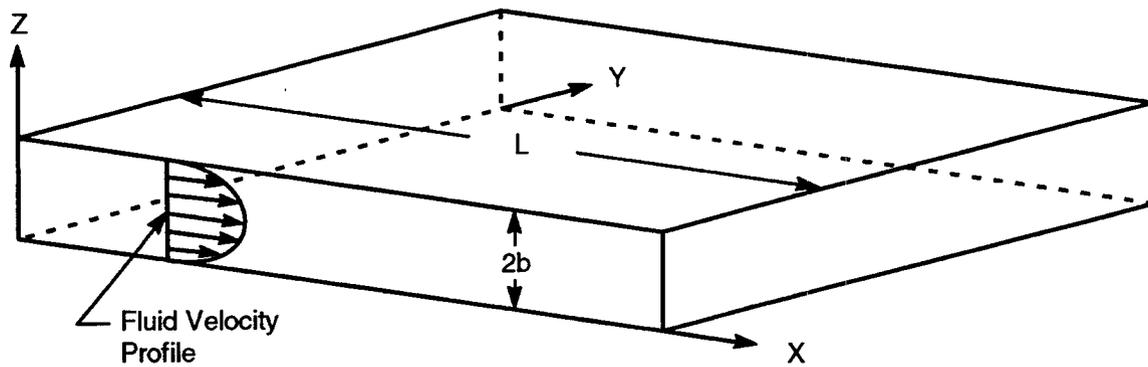


Figure 5-5. Schematic of parallel-plate channel

However, it should also be noted that the function $g(H, \tau)$ in Eq. (5-8) and the function $f(H, \eta)$, included in Eq. (5-13) below, decrease rapidly as the separation from a wall, H , increases. Therefore, in Eq. (5-8) and in Eq. (5-13), if the colloid size is very much smaller than the aperture of the channel, the effect of the top wall will be negligible as the colloid approaches the bottom wall, and vice versa.

5.4.2.3 London-van der Waals Forces

Colloid-wall interactions are also affected by the London-van der Waals attractive force, which can be expressed mathematically as

$$F_L = - \frac{2}{3} \frac{A}{a} \left[\frac{f(H, \eta)}{f_z(H)} - \frac{f(H_u - H, \eta)}{f_z(H_u - H)} \right] \quad (5-13)$$

where

- A = Hamaker constant
- $f(H, \eta)$ = London retardation function given by

$$f(H,\eta) = \{[1 + 0.620725L + 0.07519L^2] [H^2(2 + H)^2]\}^{-1} \quad (5-14)$$

for $L(=2\pi H/\eta) \leq 3$, and by

$$f(H,\eta) = \frac{[1.024172/L - 0.714228/L^2 + 0.555262/L^3]}{[H^2(2 + h)^2]} \quad (5-15)$$

for $L > 3$, where η is the electron oscillation wavelength.

Equations (5-7), (5-8), and (5-13) can be added to arrive at the sum of all the external forces acting on the colloids (Adamczyk and van de Ven, 1981)

$$F_{\text{ext}} = F_G + F_E + F_L \quad (5-16)$$

Invoking Newton's second law of motion, it can be shown that the vertical velocity of the colloids is given by (Adamczyk and van de Ven, 1981)

$$v_z = \frac{F_{\text{ext}}}{6\pi\mu a f_z(H)} \quad (5-17)$$

5.4.3 Brownian Motion

Small particles ($< 1 \mu\text{m}$ diameter) exhibit random thermal motion, more commonly known as Brownian motion. Brownian motion can cause colloids to both attach and detach from the walls of the channel through which the suspension is flowing (Ruckenstein and Prieve, 1976; Dahneke, 1975a; Adamczyk and van de Ven, 1981; Sharma and Yortsos, 1987). To date, evidence on the presence of colloids in natural environments similar to those expected or encountered at candidate HLW disposal sites indicates that, by and large, these colloids have sizes $< 1 \mu\text{m}$ (see Sections 2, 3, and 4). Therefore, an analysis of colloid transport in a PA of a HLW repository should consider particle attachment to, and detachment from, the walls of the channel due to Brownian motion.

The colloidal-wall interactions are characterized by a potential energy function (Dahneke, 1975a) (see Figure 5-3). The total energy of a colloid under Brownian motion is

$$E_T = \frac{1}{2}mu^2 + E(H) \quad (5-18)$$

where

$$E_T = \text{total energy}$$

m = mass
 u = velocity

The first term in the right-hand side of Eq. (5-18) is the kinetic energy of the particle, while the second term is the potential energy function. Typically, the potential energy has a maximum value at a distance from the wall $H=H_{\max}$ and a minimum at a distance $H=H_{\min}$ (see Figure 5-3). Colloids whose distance from the walls of the channel are in the range $H=H_{\min} \leq H \leq H_{\max}$ are considered to be attached to the wall.

Ruckenstein and Prieve (1976), using Schmulochowski's theory, in the presence of a significant potential energy barrier, and under pseudosteady-state conditions, obtained the following expressions for the rate of particle release and deposition due to Brownian motion, respectively.

$$\sigma_{\text{rel}} = D_B H_{\max} \left(\frac{e_{\max} e_{\min}}{2\pi kT} \right)^{\frac{1}{2}} \exp - \left(\frac{E_{\max} - E_{\min}}{kT} \right) \quad (5-19)$$

and

$$\sigma_{\text{dep}} = D_B H_{\max} \left(\frac{e_{\max}}{2\pi kT} \right)^{\frac{1}{2}} \exp \left(- \frac{E_{\max}}{kT} \right) \quad (5-20)$$

where

D_B = Brownian diffusivity ($= kT/6\pi\mu$)
 e_{\min}, e_{\max} = $\partial H/\partial H$ evaluated at H_{\min} and H_{\max} , respectively

In order to use Eqs. (5-19) and (5-20), the potential energy must be expressed in terms of H . Several papers in the literature have proposed such expressions (see e.g., Dahneke, 1975a; Ruckenstein and Prieve, 1976; and Guzy et al., 1983).

5.5 TRANSPORT EQUATIONS

To simulate the transport of radionuclides in PA analyses, in principle, one has to consider the movement of the radionuclides both as soluble species and as radiocolloids simultaneously, and couple the attendant equations. This process requires at least four mass balance equations represented by (i) a transport equation for dissolved species, (ii) an accumulation equation for sorbed dissolved species, (iii) a transport equation for colloids, and (iv) an accumulation equation for attached colloids, as well as the coupling terms between them. A set of these equations, in principle, is required for each dissolved species and every colloid species.

The transport equation for colloids can be written for the i^{th} species of colloids; the i^{th} species can be pseudocolloids of a specific radionuclide of a given size, real or true colloids of a specific

radionuclide of a given size, or naturally occurring groundwater colloids of a given size. If dissolved radionuclides sorbed onto the surface of naturally occurring colloids of the i^{th} species, then the latter change to a pseudocolloid of the j^{th} species. The colloid transport equation needs to account for this change, and that is one of the reasons why it is more appropriate for this equation to track the number concentration of colloids as opposed to their mass concentration.

In the development of the transport equations, it is assumed that the colloidal suspension will be sufficiently dilute so that: (i) the colloids do not interact with each other (i.e., there is no flocculation), and (ii) the colloids do not extract momentum from the flow (i.e., the flow field is at steady state and is not modified). It is also assumed that (i) the colloid's size is constant (i.e., the size of the colloids does not change due to growth, positively or negatively), (ii) the colloid transport occurs exclusively within fractures (i.e., no colloid transport within the porous matrix), (iii) the colloids do not diffuse from the fractures into the porous matrix, and (iv) the fractures can be simulated as parallel-plate channels as shown in Figure 5-5. These simplifying assumptions notwithstanding, the set of transport equations that will be developed below are highly coupled and their solution is not trivial.

5.5.1 Transport Equation for Dissolved Species

A mass balance for the dissolved species of the i^{th} radionuclide can be written as

$$\frac{\partial(C_D\theta)}{\partial t} + q_x \frac{\partial C_D}{\partial X} = \theta D_x \frac{\partial^2 C_D}{\partial x^2} - \theta \lambda C_D - \theta M_{D-S} - \theta M_{D-C} - \theta M_{MD} \quad (5-21)$$

where

- θ = volumetric water content
- C_D = concentration of the dissolved species of the i^{th} radionuclide
- q_x = Darcian flux in the longitudinal (x) direction
- D_x = hydrodynamic dispersion coefficient in the x direction
- M_{D-S} = rate of dissolved species sorbing onto the rock surface
- M_{D-C} = rate of disappearance of dissolved species into colloids
- M_{MD} = rate of diffusion of dissolved species into the rock matrix
- λ = decay rate

Depending on whether the dissolved species forms a true or real colloid or sorbs onto existing foreign colloids to form pseudocolloids, the rate M_{D-C} could take different forms. For example, it could be the rate of nucleation or condensation due to the appearance of true colloids [see Eq. (5-25)], or it could be the rate at which the dissolved species sorbs onto a foreign colloid [see Eq. (5-27)]. In either case, it provides the coupling between the transport equation for the dissolved species and the colloid transport equation [Eq. (5-25)].

5.5.2 Accumulation of Species Sorbed onto Rock Surface

The rate of accumulation of the mass of species, G , sorbed onto the rock surface is given by a simple mass balance (Patrick, 1992):

$$\frac{\partial[\rho_R G S_w (1 - \phi)]}{\partial t} = \theta M_{D-S} - \lambda \rho_R G S_w (1 - \phi) \quad (5-22)$$

Equation (5-22) is general and does not depend on the choice of sorption isotherm; however, assuming linear equilibrium between the dissolved and sorbed species (i.e., $G = k_d C_D$), it becomes

$$\rho_R (1 - \phi) S_w k_d \frac{\partial C_D}{\partial t} = \theta M_{D-S} - \lambda \rho_R k_d C_D S_w (1 - \phi) \quad (5-23)$$

where

- ρ_R = density of the rock
- k_d = distribution coefficient
- S_w = water saturation ($=\theta/\phi$)
- ϕ = porosity of the rock

Equations (5-21) and (5-23) are combined by linear superposition to give the transport equation for the dissolved species:

$$\frac{\partial C_D}{\partial t} + \frac{v_f}{R_d} \frac{\partial C_D}{\partial x} = \frac{D_x}{R_d} \frac{\partial^2 C_D}{\partial x^2} - \lambda C_D - \frac{M_{D-C}}{R_d} - \frac{M_{MD}}{R_d} \quad (5-24)$$

where

- v_f = average fluid velocity
- R_d = $1 + \rho_R k_d (1 - \phi)/\phi$

5.5.3 Population Balance for Colloids of i^{th} Species

To date, colloid transport models developed for radioactive waste disposal sites have neglected either the coupling with the dissolved-species transport equation (Bonano and Beyeler, 1985, 1987; van der Lee et al., 1993) or the effect of surface interactions between the colloids and the walls of the channel (Nuttall et al., 1991; Castaing, 1991; Hwang et al., 1990). As noted earlier, this is one reason why the impact of colloid transport in PA has not been adequately elucidated. Even though the model discussed below is based on many simplifying assumptions, which were enumerated earlier, it incorporates the aforementioned interactions and coupling that previous models have neglected. Therefore, it may be

adequate for a preliminary assessment of colloid transport, if an approach can be devised for accounting for partially saturated conditions.

The population balance for spherical colloids of the i^{th} species is (Bonano and Beyeler, 1985; 1987)

$$\begin{aligned} \theta \frac{\partial N}{\partial t} + \theta v_f \left[3 \left(\frac{z}{b} \right) F_2 - 1.5 \left(\frac{z}{b} \right)^2 F_1 \right] \frac{\partial N}{\partial x} + \theta \frac{\partial (v_z N)}{\partial z} \\ = \theta D_B \frac{\partial}{\partial z} \left(\frac{1}{\alpha} \frac{\partial N}{\partial z} \right) - \theta M_c + \theta M_r + S_c \end{aligned} \quad (5-25)$$

where

N	=	number concentration of the colloids
$F_1, F_2,$ and α	=	empirical hydrodynamic correction functions (Adamczyk and van de Ven, 1981)
v_z	=	vertical velocity of the colloids given by Eq. (5-17)
M_c	=	rate of colloid capture due to Brownian motion
M_r	=	rate of colloid release due to Brownian motion
S_c	=	rate of colloid generation

M_c and M_r can be obtained from expressions such as Eqs. (5-19) and (5-20), while S_c can include such phenomena as nucleation, which was discussed earlier, or sorption onto a foreign colloid [see Eq. (5-27)].

The term $v_f [3(z/b) F_2 - 1.5(z/b)^2 F_1]$ in Eq. (5-25) represents the velocity of the colloids in a parallel-plate channel due to Poiseuille flow. Most other analyses of colloid transport in a fractured medium, except for Bonano and Beyeler (1985, 1987) and van der Lee et al. (1993), assume that the longitudinal velocity of the colloids is identical to the fluid's average velocity. Bonano and Beyeler (1987) demonstrated that, by relaxing this assumption, the actual average velocity of the colloid front can be estimated. This average velocity can then be compared to the average velocity of the flow and the ratio of the two velocities can be determined; this ratio would be the counterpart of the R_f for dissolved species. This ratio is one of the two ingredients needed to determine if colloid transport can enhance radionuclide releases to the accessible environment, the other ingredient being the total mass of radionuclides that could be transported due to colloids.

If a radiocolloid is a true or real colloid, then the mass concentration of the specific radionuclide carried as a colloid can be estimated as

$$C_C = N \rho_{RN} V_C \quad (5-26)$$

where

$$\begin{aligned} C_C &= \text{concentration} \\ \rho_{RN} &= \text{density of the radionuclide} \\ V_C &= \text{volume of the colloid} \end{aligned}$$

In this case, S_c in Eq. (5-25) is a function of M_{D-C} . If the radiocolloid is a pseudocolloid, then the mass of the radionuclide is primarily adsorbed to the surface of the colloid, and thus the mass concentration of the radionuclide is estimated from the expression

$$\frac{dC_C}{dt} = M_{D-C} \quad (5-27)$$

where

$$M_{D-C} = \text{function of both } N \text{ and the surface area of a colloid, } A_c$$

If one assumes that, in the case of a pseudocolloid, sorption is described by a linear isotherm, $C_C = k_{dc} C_D$, Eq. (5-27) becomes

$$k_{dc} \frac{dC_D}{dt} = M_{D-C} \quad (5-28)$$

where

$$k_{dc} = \text{distribution coefficient between the dissolved species and the foreign colloid on which the species sorbs}$$

In this case, Eq. (5-28) can be substituted into the transport equation for the dissolved species, Eq. (5-24), and the latter becomes

$$R_{dc} \frac{\partial C_D}{\partial t} + \frac{v_f}{R_d} \frac{\partial C_D}{\partial x} = \frac{D_x}{R_d} \frac{\partial^2 C_D}{\partial x^2} - \lambda C_D - \frac{M_{MD}}{R_d} \quad (5-29)$$

where

$$R_{dc} = (1 + k_{dc}/R_d)$$

5.5.4 Population Balance for Captured Colloids

The population balance equation for captured colloids has been given by Dahneke (1975a) and can be written as

$$\frac{dN_C}{dt} = M_C - M_R \quad (5-30)$$

where

$$\begin{aligned} N_C &= \text{number concentration of captured colloids} \\ M_C &= \text{rate of capture} \\ M_R &= \text{rate of release} \end{aligned}$$

Equation (5-30) simply describes the accumulation rate of colloids at the walls of the channel as the difference between the rate of capture and the rate of removal from the wall. The mass of radionuclides contained by the captured colloids can be calculated either with Eq. (5-26) in the case of true colloids or with Eq. (5-27) for pseudocolloids.

5.5.5 Sample Results of Previous Colloid Transport Analysis

As explained earlier, Bonano and Beyeler (1985, 1987) performed simple analyses of colloid transport in single fractures. Herein, we present sample results from Bonano and Beyeler (1987); the purpose of presenting these results is to demonstrate that (i) sensitivity analyses can be performed to identify critical data needs, and (ii) auxiliary analyses can be performed to provide a foundation for PA analyses of coupled colloid/soluble species transport. The results herein presented should not be construed as definitive.

Bonano and Beyeler (1987) solved, in dimensionless form, the equivalent of Eq. (5-25). They calculated the Sherwood number for colloids crossing from Region I to Region II, as shown in Figure 5-4. The Sherwood number, Sh , is defined as

$$Sh = (1/\alpha) (b/N_0) [\partial N/\partial z]_{z = \delta} \quad (5-31)$$

where

$$\begin{aligned} \alpha &= \text{empirical hydrodynamic correction function (Adamczyk and van de Ven, 1981)} \\ b &= \text{half-width of channel} \\ N &= \text{number concentration of colloids} \\ N_0 &= \text{number concentration of colloids at } x = 0 \text{ (channel entrance)} \\ z &= \text{distance from the bottom wall of the channel} \\ \delta &= \text{boundary between Region I and Region II (see Figure 5-4)} \end{aligned}$$

Sh denotes the rate at which colloids move from Region I to Region II and, as such, is a quantitative indication of the rate at which colloids are captured because, as discussed earlier, colloids within Region II are assumed to be captured and not available for transport.

Figure 5-6 is a plot of Sh as a function of dimensionless axial position, ξ ($= x/b$), along the parallel-plate channel assumed by Bonano and Beyeler (1987) to represent a fracture. Also shown in this figure is the effect of the width of the colloid-size distribution denoted by the value of D_R ; the larger the value of D_R , the wider the colloid size distribution. This figure shows that (i) the rate of colloid capture is higher near the entrance of the channel, and (ii) that the narrower the size distribution, the higher the capture rate. These results suggest that higher colloid retention rates will occur near the source of the colloids where the number concentration of colloids is higher. However, explaining the impact of size distribution on the retention rates will require a more careful analysis.

Figure 5-6 is accompanied by a plot of dimensionless average colloid-front velocity in Figure 5-7. The average colloid-front velocity is rendered dimensionless by normalizing the average colloid velocity by the average fluid velocity; therefore, the numerical value of the dimensionless average colloid-front velocity indeed indicates how fast colloids travel with respect to the suspending fluid. Figure 5-7 shows that, as colloids are removed from the flowing suspension, the average velocity of the colloids remaining in suspension increases. This increase in velocity is a direct impact of the hydrodynamic chromatography effect discussed earlier in this section. At every axial position in the channel, the average colloid-front velocity is higher than the average velocity of the fluid, eventually becoming 15 percent higher than the latter. However, it is noted that this increase in the average colloid-front velocity is the result of colloids being captured and removed from suspension. Therefore, the release of radionuclides from a HLW repository needs to address both the higher average colloid velocity and the total amount of radioactivity that can be released as colloids.

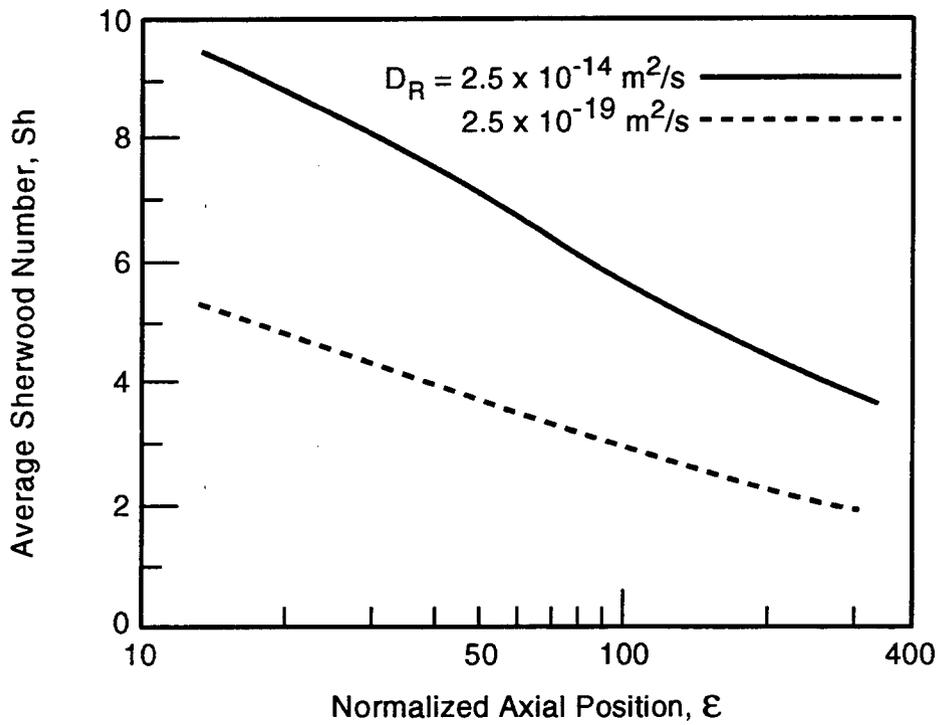


Figure 5-6. Plot of Sherwood Number (dimensionless colloid capture rate) as a function of axial position along fracture (Bonano and Beyeler, 1987)

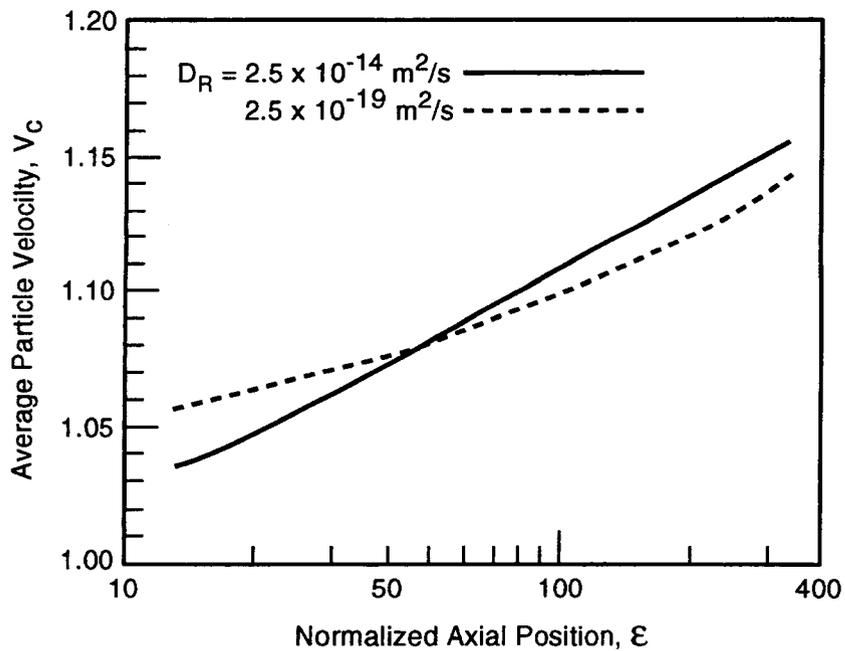


Figure 5-7. Plot of dimensionless average colloid-front velocity as a function of axial position along fracture (Bonano and Beyeler, 1987)

6 CONCLUSIONS

Several sources and processes can be identified as origins of colloids at a HLW repository. These processes include: leaching of vitrified wasteforms and spent fuel, corrosion of EBS (principally, waste package and backfill, if used), interactions with other human-introduced materials during construction and operation of the repository, and precipitation processes as a result of thermal gradient over the repository site. In addition, colloids may be generated by the interaction between radionuclides in suspension and exposed geologic media. Such a process is largely determined by the chemical properties of the system. The formation of radiocolloids from the vitrified wastes and spent fuel in a geologic repository depends on the chemical state of the individual elements (e.g., degree of hydrolysis, and formation of organic and inorganic complexes, etc.). Formation of colloids in the groundwater would be generally more favorable for actinides in their lower oxidation states, as compared to fission products, because of solubility constraints. Colloids of such actinides could be present in the groundwater. The colloidal particles may be poorly sorbed on water-exposed geologic media in comparison with radionuclides in solution, the concentration of which is governed by their solubility limits. The initial concentration of radionuclides in solution, in the vicinity of the waste package depends on a number of variables, including the solubility limits of the different species. Lower solubilities can lead to enhanced formation of colloids. As a result, the measured solubilities of actinides in near-neutral solutions could be much greater than the thermodynamically estimated values. Colloid transport may offer a faster mechanism, as compared to soluble species, for release of radionuclides from the EBS to the geosphere and from the geosphere to the accessible environment. Consequently, PA models that rely on the solubility limit as the extent to which actinides can exist in repository groundwaters could underestimate the potentially transportable radionuclides to the repository far field. Therefore, failure to consider colloid transport as a radionuclide transport mechanism could underestimate radionuclide releases to the accessible environment and undermine demonstration of compliance with the requirements in 10 CFR Part 60.

Field studies in the Yucca Mountain vicinity and at other analog sites demonstrate that natural colloids and organic matter are present in significant amounts under some conditions ($> 1 \text{ mg} \cdot \text{L}^{-1}$). Natural heterogeneities and difficulties in field sampling for colloids, however, make it hard to unambiguously determine the amounts of colloids present in the subsurface. Many of these particles are sorptive (clays, oxyhydroxides), but the stability of the colloid suspension and the sorption behavior of the actinides on these are both strongly affected by changes in chemical conditions such as pH and ionic strength. For example, particle stability may decrease under low pH conditions due to electrostatic attraction; under the same conditions, actinide sorption is likely to be low. Under high pH conditions, carbonate particles may be stable, but actinide desorption is likely due to the presence of ligands such as CO_3^{2-} , making pseudocolloid formation less significant. In addition, colloids have been identified in dissolution experiments involving unirradiated spent fuel and vitrified wasteforms. These processes also seem to be a function of system chemistry, although there is considerable uncertainty in the magnitude of many of these effects.

Most of the available information on colloids is for saturated zone hydrology. It is still uncertain to what degree the colloids in the hydrologically saturated zone reflect the conditions in the unsaturated zone. Transport of colloids under unsaturated conditions is poorly understood, and only recently have laboratory methods been developed to address these issues (Wan and Wilson, 1994). Preliminary porosimetry data at Yucca Mountain suggests that matrix transport of colloids will be limited but that fracture apertures are large enough to allow colloid transport by fracture flow.

The key reason for considering colloids is the extent to which they will contribute to overall radionuclide transport to the accessible environment. If the colloid concentration is significant, and if radionuclide sorption onto the colloids is relatively high, then the contribution of colloid transport to radionuclide migration may be significant and these effects should be included in performance assessment calculations. Based on the available literature, it may be possible for colloids to form in the Yucca Mountain environment, but the extent to which they could contribute to overall radionuclide transport remains unclear. Mathematical models currently exist that can simulate colloid transport for idealized systems. However, these models typically rely on a number of empirical parameters that are either poorly known or difficult to measure for natural systems, and they do not explicitly consider the effects of system chemistry on colloid formation and stability. Some geochemical models exist to take into account some of this dependence, but they have not yet been modified to consider colloid transport.

It is recognized that very limited experimental data related to colloid transport in unsaturated environments are available, particularly that applicable to the Yucca Mountain site. Therefore, any performance assessment exercise conducted at present would require a considerable number of assumptions about the magnitude of parameters necessary for the development of the PA model. Verification of the assumed magnitude of the parameters will have to await experimental investigations. Based on the literature reviewed for this report, there appears to be a need to conduct additional experimental investigations to obtain data that would be needed for verifying assumptions in the current models and for developing advanced models for performance assessment of the repository. Areas requiring additional experimental information or data include:

- Conditions for colloid stability (e.g., size and charge of colloids, ionic strength, and pH of solution)
- Dynamic balance of processes such as colloid formation, flocculation, escape or transport by groundwater flow, disintegration, and sedimentation
- Formation kinetics of colloids from secondary phases
- Influence of container and waste package materials corrosion on formation and stability of colloids
- Colloid sorption and trapping in rock matrix and fracture paths
- Colloids formation and transport under unsaturated repository conditions

The evidence to date seems to suggest that colloid transport could be important; however, a systematic analysis to determine the relative importance of colloid transport has yet to be conducted. The equations presented in Section 5 of this report have only been applied in fairly simple analysis of colloid transport under fully saturated conditions. Therefore, KTUs identified at the beginning of this report remain unresolved. Whether colloids represent a potentially important means for transport of radionuclides in the Yucca Mountain environment, in comparison to transport as dissolved species, is still uncertain. The effect on, and approach to, modeling of colloid transport under partially saturated conditions is not known.

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