

**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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September 1995

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ABSTRACT

Recent publications have suggested that radionuclides may be released from high-level radioactive wastes (HLW) in the form of colloids. Also, the possibility exists that radionuclides dissolved in groundwater could sorb onto naturally occurring colloids or those resulting from human-introduced materials. If significant amounts of radionuclides can be released from the HLW (spent fuel and vitrified waste) in colloidal form, radionuclide transport models may need to be modified to include colloid transport processes. The transport models also need to account for radiocolloids that may result from interactions between natural colloids or colloids formed from human-introduced materials and the radionuclides in solution in the groundwater. The current state of knowledge regarding the formation and transport of radioactive colloids at a HLW repository site does not allow a definitive conclusion of the role and impact of colloid transport on repository performance. This report documents a review of the literature related to the formation and transport of colloids potentially relevant to HLW geologic disposal, particularly at the proposed Yucca Mountain HLW repository site. The reviewed information was examined in the context of the requirements in the Nuclear Regulatory Commission (NRC) regulation for HLW disposal (10 CFR Part 60). Based on the insights gained, recommendations for future colloid-related work are provided.

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ABBREVIATIONS AND ACRONYMS

CDM	Compliance Determination Methodology
CDS	Compliance Determination Strategy
CNWRA	Center for Nuclear Waste Regulatory Analyses
COOH	carboxylic acids
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
FOC	fixed organic carbon
GWTT	groundwater travel time
HLW	high-level [radioactive] waste
IPA	iterative performance assessment
KTU	key technical uncertainty
LA	license application
LANL	Los Alamos National Laboratory
LARP	License Application Review Plan
MTHM	metric ton heavy metal
MW	molecular weight
NAS	National Academy of Sciences
NMSS	Office of Nuclear Material Safety and Safeguards
NOM	natural organic materials
NRC	Nuclear Regulatory Commission
NTS	Nevada Test Site
PA	performance assessment
PAC	potentially adverse condition
pH _{ZPC}	pH value at the zero point of charge
R _f	retardation factor
SA	surface area
SA/V	surface area to volume ratio
SEM	scanning electron microscopy
SWL	static water level
TEM	transmission electron microscopy
TDS	total dissolved solids
TOC	total organic carbon
YM	Yucca Mountain
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

Colloids are small "particles" that are larger than dissolved species. They range in size from 10^{-5} to 10^{-9} meters. For years many publications have suggested that long-lived radionuclides (actinides) may be released from high-level waste (HLW) as colloids, or that radionuclides in solution could sorb onto naturally occurring colloids in the geologic setting at a repository site. To date, performance assessment (PA) models developed to evaluate the overall performance of a HLW geologic repository generally consider only the transport of dissolved species. If, at a particular HLW site, significant amounts of radionuclides can be released from HLW or can be transported in the form of colloids, PA models may need to be modified to include colloid formation and transport processes. This report reviews and examines the literature related to the formation and transport of colloids and was undertaken to provide information related to colloids, their potential role in the release of radionuclides from the waste form, and their role in the transport of radionuclides through the geologic setting. In addition, it is considered an important step in identifying regulatory and compliance concerns, providing the basis for interactions and preclicensing guidance with the U.S. Department of Energy (DOE), and developing a technical data and information base to aid the Nuclear Regulatory Commission (NRC) in the review of a license application.

The potential sources of colloids at the proposed HLW repository at Yucca Mountain (YM), Nevada, are naturally occurring groundwater colloids, engineered barrier system (EBS) corrosion products, vitrified wasteforms and spent fuel, and materials introduced during construction such as concrete and clays. Groundwater samples collected in the vicinity of the proposed YM repository show natural colloid concentrations to be in the $0.27\text{--}135\text{ mg}\cdot\text{L}^{-1}$ range. Although this level of colloid concentration can be considered low on a mass basis, colloids could play a significant role in the transport of radionuclides because of the high specific surface area they provide for sorption or precipitation of dissolved radionuclides. Furthermore, a variety of hydrogeochemical perturbations typically found at waste sites or other contaminated areas have been associated with increased concentrations of colloids in groundwater. For example, changes in temperature, ionic strength and composition, redox conditions, pH, dissolved organic carbon (DOC), recharge conditions, the introduction of chemicals or engineering materials (e.g., grout) to a formation, or waste form degradation have all been associated with the formation or mobilization of colloids in groundwater. The potential for similar perturbations to form or increase the concentration of colloids at the YM site cannot be completely evaluated based on the limited information currently available.

The PA requirements of the NRC regulation 10 CFR Part 60 and those of the U.S. Environmental Protection Agency (EPA) (40 CFR Part 191)¹ related to cumulative releases of various radionuclides over the 10,000-yr post-closure period, included by reference in 10 CFR 60.112, do not distinguish between radionuclides released to the accessible environment as dissolved species, colloids, or gasses. However, 10 CFR 60.122 does require characterization of the various forms in which radionuclides may be released and transported. Thus, 10 CFR Part 60 ensures that all potentially significant forms of radionuclide releases will be included in any demonstration of compliance with the requirements of 10 CFR 60.112. Consequently, DOE is required to address and evaluate the potential significance of radionuclides in colloidal form.

¹ 40 CFR Part 191 was vacated by the U.S. Court of Appeals in 1987 and remanded to the EPA for revision and repromulgation. To date, the EPA has not repromulgated a regulation for disposal of HLW and spent fuel. For the purpose of this report the requirements contained in the 1985 version of 40 CFR Part 191 have been used as a reference point.

Based on an analysis of 10 CFR Part 60, a number of technical uncertainties related to HLW disposal at the proposed YM site have been identified in the development of the NRC License Application Review Plan (LARP) (Nuclear Regulatory Commission, 1994). Ten technical considerations called key technical uncertainties (KTUs), have been identified that are directly or indirectly related to colloid formation and transport. These KTUs are

- The ability to project the nature and rates of quaternary geochemical processes
- The identification of geochemical conditions that would inhibit particulate and colloid formation
- The characterization of the geochemistry of the partially saturated hydrologic zone
- The effects of degree of saturation on geochemical processes, such as colloid formation and sorption, on the transport of radionuclides
- The parametric representation of retardation processes
- The identification of processes concerning retardation of radionuclides
- The identification of processes adversely affecting the engineered barrier system (EBS)
- The magnitude of the effects of geochemical processes on radionuclide retardation
- The identification of potential adverse effects of geochemical processes on the EBS performance
- The ability to predict release of radionuclides from waste packages

Given the breadth and complexity of scientific understanding needed to address these KTUs, much work seems to lie ahead for DOE before a credible and defensible conclusion can be reached on the significance of colloid formation and transport to the performance of a HLW repository. Based on the results of this review, future NRC research or technical assistance support may be warranted to address each of the KTUs in order to develop adequate review capabilities and review plans needed to evaluate DOE colloid formation and transport analysis as well as their associated PA calculations. However, this literature review and analysis suggests that the highest-priority KTUs related to colloids are

- The identification of geochemical conditions that would inhibit particulate and colloid formation
- The effects of degree of saturation on geochemical processes, such as colloid formation and sorption, on the transport of radionuclides
- The parametric representation of retardation processes

1 INTRODUCTION

Colloid formation and transport at a high-level radioactive waste (HLW) repository as a possible means for the fast transport of radionuclides through the engineered barrier system (EBS), the geologic setting, and into the accessible environment has been a subject of considerable debate within the waste management technical community. Numerous research efforts since the late 1970s and early 1980s related to colloid formation and transport at radioactive waste disposal and other contaminated sites notwithstanding, the issue still remains an open one. Lack of generic and site-specific data under relevant groundwater conditions at a HLW repository site as well as a lack of understanding of the phenomena and processes governing colloid formation and transport have precluded the development of calculation models and tools suitable for performance assessment (PA). As a result, it is unknown if radionuclide transport as colloids needs to be included in estimates of the long-term performance of HLW repositories.

1.1 PURPOSE AND SCOPE OF REPORT

The purpose of this report is to document a study conducted to gain a better appreciation of the current state of knowledge pertaining to colloid formation and transport in geologic environments, in general, and under conditions representative of HLW repositories, particularly the Yucca Mountain (YM) site in Nevada. The relevant colloid literature in the context of a HLW repository site was reviewed and examined. The literature review identified colloids that could influence the migration of radionuclides in a repository environment and the behavior of colloids that would be important to assess performance of the repository in the post-containment period. The results of the study could be used as the basis for making decisions regarding: (i) if colloids present a possible mechanism for faster transport and earlier release of radionuclides to the accessible environment as compared to transport of dissolved species, and (ii) studies or investigations that should be undertaken related to colloid formation and transport. The information contained in this report should provide a basis for the Nuclear Regulatory Commission (NRC) to determine future work that should be undertaken related to colloids at a HLW repository, specifically work that pertains to PA and to the development of compliance determination methods (CDMs). Finally, the results of the study herein documented could be used by NRC staff in the development of guidance for the U.S. Department of Energy (DOE) regarding the latter's site characterization program at YM.

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 key technical uncertainties (KTUs) in the regulatory requirements related to colloid formation and transport. Applicability of current data to PA needs can be used to identify additional KTUs that require further investigation. This report concludes with recommendations. This report should be considered as an important 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 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.

It is beyond the intended scope of this report to provide a detailed analysis of the effects of degradation products of waste package materials, construction materials, and other human-introduced materials (e.g., diesel fuel, lubricants, etc.). In addition, the relative impact of different wastefoms (glass versus spent fuel) is not addressed in detail. Although only a small fraction of this total radionuclide inventory will be in glass, if actinide releases associated with colloids are greater during glass leaching,

it may become important in PA. Detailed consideration of these issues will depend on ultimate repository design and inventory.

1.2 BACKGROUND INFORMATION

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 10^{-5} to 10^{-9} m-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; Stumm and Morgan, 1981). Colloids can be formed from both inorganic and naturally occurring organic materials from a variety of sources (McCarthy and Zachara, 1989; McCarthy and Degueldre, 1993). 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 unique 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, 1995; Ahn et al., 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 implicit assumption in this solubility-limited approach is that colloids are not formed or that they play an insignificant role in radionuclide release. It should also be noted that the term "solubility" is, for many reasons, an ambiguous description, particularly for M(III) or M(IV) ions in natural aquatic systems. The concentration of a given actinide ion, either complexed or noncomplexed, depends on its chemical state. The new solid phase of the actinide ion is often a multicomponent phase for which the solubility parameters are poorly understood. Furthermore, the solubility limits of complexed species can range over many orders of magnitude. Laboratory experiments show that release of actinides (e.g., Pu and Am) from vitrified wastefoms can occur predominantly via colloids (Bates et al., 1992b). The results of a recent study on vitrified wastefoms, 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 released as colloidal particles (Bates et al., 1992a). These concentrations are valid only for the experimental conditions used in the particular test (Bates et al., 1992a), and are likely to be much lower in natural systems, in the presence of EBS materials.

It should be noted that the susceptibility of a particular species of radionuclides to form colloids is a strong function of the chemical state of the species. Other studies 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). 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

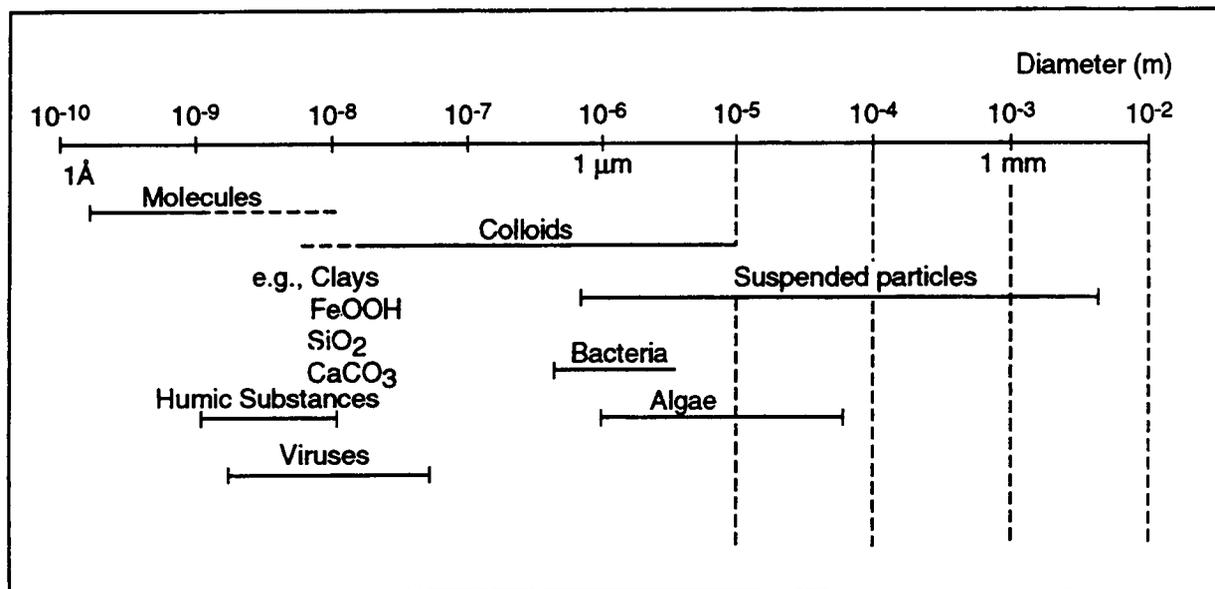


Figure 1-1. Size spectrum of water-borne particles (adapted from Stumm and Morgan, 1991)

the 25- to 450-nm-size range (Nelson and Orlandini, 1986; Penrose et al., 1990). The results of such studies lead to the conclusion that repository performance models, which assume maximum release of actinides to be limited by the solubility limit in groundwaters, particularly for Pu and Am 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 the presence of radionuclides in colloidal form could lead to an increase in the releases to the accessible environment beyond the permissible limit during the 10,000-yr regulatory period following permanent closure of the repository.

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

This section discusses the regulatory requirements related to the geologic disposal of vitrified wastes 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 to the accessible environment of radionuclides over 10,000 yr following repository closure.

1.3.1 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).

In 10 CFR 60.113, the performance requirements for the EBS and geologic setting subsystems of the repository system are stipulated. The EBS performance requirement [10 CFR 60.113(a)(1)] consists of: (i) a containment requirement for the HLW packages, and (ii) a radionuclide release rate limit for 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)(ii)(B)]. 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 60.113(a)(2), travel time along the fastest path for radionuclide migration to the accessible environment is to be more than 1,000 yr.

1.3.2 U.S. Environmental Protection Agency Standard

As stipulated in the Nuclear Waste Policy Act of 1982, as amended, the NRC regulation 10 CFR Part 60 incorporates by reference (in 10 CFR 60.112) standards developed and promulgated by the EPA for the disposal of HLW. Such standards are incorporated by reference in 10 CFR 60.112. In 1985, the EPA promulgated a set of HLW standards in 40 CFR Part 191, however, these standards were vacated by the U.S. Court of Appeals in 1987 and remanded to the EPA for reexamination, revision (if necessary), and reissue.

The Energy Policy Act of 1992 instructed the EPA to commission a study by the National Academy of Sciences (NAS) to suggest appropriate and practically implementable standards for the proposed HLW repository at YM. The EPA would then act on NAS suggestions and repromulgate standards for the proposed YM repository. Such standards have not been promulgated by the EPA. Therefore, the 1985 version of the EPA HLW standards was used as the basis for radionuclide releases to the accessible environment.

Table 1-1 of 40 CFR Part 191 (U.S. Environmental Protection Agency, 1985) lists release limits for radionuclides stipulated under the Containment Requirements in 40 CFR 191.13. These requirements do not differentiate between radionuclide releases as dissolved species or as colloids; rather, total releases of radionuclides to the accessible environment—whether as dissolved species, gaseous form, or colloids—over the 10,000-yr period following closure of a HLW repository need to be considered. Thus, the impact of colloid formation and transport on the radionuclide releases needs to be ascertained.

Other requirements in 40 CFR Part 191, such as the Groundwater Protection Requirements (40 CFR 191.15) and the Individual Protection Requirements (40 CFR 191.16), could also be affected by the transport and release of radionuclides as colloidal particles.

1.4 RELATIVE IMPORTANCE OF RADIONUCLIDES IN THE HIGH-LEVEL WASTE

The anticipated contribution of various radionuclides to the total inventory for spent fuel and vitrified wastefrom 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 fission

Table 1-1. Limits for cumulative releases to the accessible environment for 10,000 yr after disposal (adapted from U.S. Environmental Protection Agency, 1985)

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	

product ^{129}I is important but is not shown in the tables because its contribution to the total inventory is small (<0.1 percent in fuel and <0.03 percent in glass).

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 60.113(a)(1)(ii)(A)]. 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. Radionuclides contributing more than 0.1 percent to repository inventory for pressurized water reactor 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 ^a	24%	²⁴⁰ Pu	27%	²⁴⁰ Pu	39%	⁹⁹ Tc	17%
⁹⁰ Sr	17%	²³⁹ Pu	17%	⁹⁹ Tc	3%	⁵⁹ Ni	4%
⁹⁰ Y ^b	17%	²⁴³ Am	0.9%	²⁴³ Am	1%	⁹³ Zr	3%
²⁴¹ Am	9%	²³⁹ Np ^c	0.9%	²³⁹ Np ^c	1%	^{93m} Nb ^d	3%
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 ^d	0.4%	²³³ Pa ^e	2%
⁶³ Ni	0.8%	^{93m} Nb ^d	0.1%	²⁴² Pu	0.4%	²²⁶ Ra ^f	2%
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.

1.5 COLLOID-RELATED 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).

One goal of the development of KTUs 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 NRC safety reviews of the pertinent portions of the DOE license application. These strategies and the related KTUs have been

Table 1-3. Radionuclides contributing more than 0.03 percent 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 ^a	24%	²³⁹ Pu	28%	²⁴⁰ Pu	13%	⁹³ Zr	11%
¹³⁷ Cs	24%	²⁴⁰ Pu	16%	⁹⁹ Tc	11%	^{93m} Nb ^c	11%
^{137m} Ba ^b	22%	⁵⁹ Ni	6%	⁵⁹ Ni	11%	⁵⁹ Ni	8%
²³⁸ Pu	3%	⁹⁹ Tc	6%	⁹³ Zr ^c	7%	²³⁴ U	6%
⁶³ Ni	0.7%	⁹³ Zr	3%	^{93m} Nb	7%	²³⁹ Pu	6%
¹⁵¹ Sm	0.7%	^{93m} Nb ^c	3%	²³⁴ U	5%	²³⁰ Th ^d	4%
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.

published by the NRC as a part of the License Application Review Plan (LARP) (Nuclear Regulatory Commission, 1994). The technical concerns expressed in these KTUs must be addressed by the DOE in its license application.

The NRC is conducting, and intends to continue, precicensing reviews of DOE data and analyses, NRC-sponsored confirmatory research, iterative performance assessment (IPA), and interactions with the DOE. As a result of these pre-licensing activities, the list of KTUs is continuously reviewed for addition, deletion, and/or revision as it becomes necessary. For example, uncertainty remains regarding the influence of 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. The human-introduced materials will include both inorganic materials such as cements, clays, and metals, and organic (or organic-bearing) materials such as water, polymers, lubricants, oils, etc. These materials have the potential for both generating colloids and acting as nuclei for pseudocolloids. (This subject is discussed further in Section 2.5.) Safety review plans and methodologies are currently being formulated.

The current KTUs related to colloid formation and transport, selected from the regulatory requirements and published in the LARP (Nuclear Regulatory Commission, 1994), are described and discussed in subsequent sections.

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

The nature and rates of geochemical processes that either would not affect or would affect favorably the ability of the geologic repository to isolate waste [10 CFR 60.122(b)(2)] is considered a favorable condition. Colloid formation and transport 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 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.

The assessment of the role of colloids in a geologic repository cannot be limited to consideration of the colloids at the site under undisturbed conditions. Compliance with the regulations must reflect the potential for generating new types or increased concentrations of colloids by alteration of geochemical conditions as a result of disturbances arising from the near-field environment. For example, the hyperalkaline front emerging from a degrading shaft backfill may produce colloids, as will the redox front moving away from a corroding carbon steel overpack for the waste canister. The redox front may extend through an EBS backfill into the host rock. In addition to localized effects associated with the repository, global climatic changes could affect ionic strength and composition of recharge water and inputs of organic matter. Although the materials of construction (repository, waste package, and the backfill) can be selected with relative ease, the quantification of the consequences of their degradation under a difficult-to-predict geologic environment results in considerable uncertainty with respect to formation and stability of colloids and the transport of radionuclides via colloids.

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

Geochemical conditions that would inhibit the formation of colloids or the transport of radionuclides by particulates and colloids [10 CFR 60.122(b)(3)(ii)-(iii)] are also considered to be favorable conditions. Different factors 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 wastefrom 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 a geologic system such as the unsaturated zone at YM could create significant amounts of particulate material. Since many dissolved radionuclides are strongly attracted to solid surfaces, radionuclides attached to particles moving with groundwater 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. The contribution of surface interactions to the overall energetics of the system studied becomes more important for smaller particles and colloids. Lacking thermodynamic and kinetic data on these phases, it is difficult to predict their effect on performance of the repository. Existing codes may need to be modified to take into account the effect of surface charge 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 5.2.1.1, Table 5-1.) If coupled flow and transport modeling is attempted, consideration of the effect of particle size on diffusivity and rate of gravitational settling at various flow rates would be required. Also, experimental data on the surface charge of phases expected at the repository site would be needed.

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

Geochemical conditions that would inhibit the formation of colloids or the transport of radionuclides by particulates and colloids [10 CFR 60.122(b)(3)(ii)-(iii)] are considered to be favorable conditions. 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. In addition to the averaged geochemical composition effects, supersaturation in localized regions of the repository (e.g., vicinity of the waste package) has the potential for colloid formation. The effect of colloids advected away from the localized regions is unknown and may be difficult to quantify in the absence of *in situ* tests.

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 Bergfeldt, 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 YM is, therefore, extremely uncertain.

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

As discussed in 10 CFR 60.122(b)(3)(ii)-(iii), geochemical conditions that would inhibit the formation of colloids or the transport of radionuclides by particulates and colloids are considered to be favorable to performance of the geologic setting. The proposed repository location is in a hydrologically partially saturated horizon underneath YM. 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 is the effect of degree of saturation 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 YM are favorable or unfavorable for inhibition of transport of radionuclide. The unsaturated environment may not necessarily influence colloidal transport in the same way as the dissolved species.

1.5.5 Parametric Representation of Retardation Processes Involving Radionuclide-Bearing Particulates, Colloids, and Complexes

Favorable conditions include geochemical conditions that would inhibit the formation of colloids or the transport of radionuclides by particulates and colloids [10 CFR 60.122(b)(3)(ii)-(iii)]. 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.

1.5.6 Uncertainty in Identifying Geochemical Processes That Reduce Radionuclide Retardation

Geochemical processes that would reduce radionuclide retardation are considered to be potentially adverse conditions (PACs) [10 CFR 60.122(c)(8)]. Identifying those geochemical processes whose contributions to the existence of this PAC are, respectively, likely, unlikely, or uncertain, can be used to assign the appropriate level of review. Those processes that are unlikely to contribute to the PAC are assumed to be unlikely to affect performance. Thus, technical uncertainties with regard to those processes would not be "KTUs." Compliance with this regulatory requirement topic will require a quantitative evaluation of the effect of each of the processes on radionuclide retardation. These processes involve both radioactive and nonradioactive constituents of the repository and vicinity. The number of chemical components present at YM to be considered in this analysis will include key radionuclides and components introduced in the construction and characterization of the repository, corrosion products from the EBS, and components indigenous to the system. Geochemical modeling likely to be used for demonstrating compliance with this regulatory requirement topic involves the simultaneous solution of linear and nonlinear equations representing mass balance and mass action, respectively, of the chemical components. The large number of components, processes, and conditions expected at the site precludes quantitative characterization of all possible (and expected) combinations of these parameters. Indications are that the DOE will use the minimum K_d approach to calculate radionuclide retardation (Meijer, 1992). This simplifying approach combines some experimental data with assumptions on water-rock interactions. As a result, there is a risk that some important geochemical processes will not be characterized quantitatively.

1.5.7 Uncertainty in Identifying Processes That May Adversely Affect the Engineered Barrier System

The presence of geochemical processes that would adversely affect the performance of the EBS [10 CFR 60.122(c)(8)] is considered a PAC. The colloids may form through the degradation of the different components of the EBS (waste package, spent fuel, vitrified wastes). Currently, the design concepts include the use of carbon steel for the waste package construction. This material is known to form colloids when placed in contact with groundwaters. Other colloid-forming materials, such as concrete and clays, may be used in the EBS as backfill material or material to stabilize the drifts formed for the emplacement of the waste package. 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.

1.5.8 Uncertainty in Identifying the Magnitude of the Effects of Geochemical Processes That Reduce Radionuclide Retardation

One PAC is the presence of geochemical processes that would adversely affect the retardation of radionuclides [10 CFR 60.122(c)(8)]. 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 groundwater flow and colloid formation and transport. Experimental data or field observations that can be used to identify processes may also be useful in identifying and quantifying important parameters for modeling the magnitude of the effects of these processes on radionuclide retardation.

1.5.9 Uncertainty in Identifying the Magnitude of Potentially Adverse Effects of Geochemical Processes on Engineered Barrier System Performance

Geochemical processes that would adversely affect the performance of the EBS [10 CFR 60.122(c)(8)] are considered PACs. The arguments for this KTU 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. Because of the strong interrelationship, a number of processes in a geologic repository may need to be coupled to quantify the consequences in a conservative manner. Coupling of two processes with uncertainties may lead to even greater uncertainty in the consequences of the coupled process. For example, microbial activity and geochemical processes, as applicable to a geologic repository, are both not fully understood and have uncertainties associated with quantification of their influence on the long-term performance of the repository. The coupled microbial-geochemical process is likely to be even more complex and may have more uncertainties associated with it. As a consequence, compliance determination for the coupled process may be much more difficult.

1.5.10 Prediction of the Releases of Nongaseous Radionuclides from Waste Packages During the Containment Period and from the Engineered Barrier System During the Post-Containment Period

Although not specifically mentioned in 10 CFR 60.113(a)(1), the formation and transport of colloids may contribute to the controlled release requirements outlined for the EBS. 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.

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^{-5} to 10^{-9} 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 necessarily correct in a scientific sense, has been retained in this report for the sake of consistency with the relevant HLW 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 hydrolyzed actinide ions, and pseudocolloids are generated by sorption of actinide ions, or colloids, on groundwater colloids. The three kinds of colloids are distinct 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, hydrolyzed precipitates of mixed metal ions, 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 generally requires ultrafiltration techniques or ultracentrifugation (Kim, 1993). Groundwater colloids are often chemically surface-active and, depending on system chemistry, may adsorb metal ions of higher charge ($\geq 2+$) 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 typically favored with increasing pH for dilute (low-ionic-strength) solutions. In the case of highly charged, redox-sensitive species such as actinides (Maiti et al., 1989; Choppin and Mathur, 1991), the pH range favoring real colloid formation is also dependent on oxidation state. For example, 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 polymerization, condensation, and precipitation is favored for the actinides in lower valence states.

2.1.3 Pseudocolloids

In contrast to real or true colloids, pseudocolloids are formed when the radionuclides sorb on natural colloids 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 such as naturally occurring organic compounds (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 hydrolyzed (Righetto et al., 1988). 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 transport 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) Water Well 20 groundwater (Kingston and Whitbeck, 1991; Buddemeier and Hunt, 1988). 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 radionuclides to transport in the repository far field due to migration of natural colloids on which they are adsorbed.

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 compounds had signatures which indicated humic and fulvic acids as well as contaminations by pumping oil or fingerprints. 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 minerals 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-mg $\cdot \text{L}^{-1}$ range, and the colloid size to be in the 1.0- to 0.03- μm range. Based on the average concentration data, the following estimation can be made: the particle population range is from $5 \times 10^8 \text{ L}^{-1}$ (minimum) to $5 \times 10^{13} \text{ L}^{-1}$ (maximum) with an average population of $1.1 \times 10^{10} \text{ L}^{-1}$ (arithmetic mean), or $2.2 \times 10^{11} \text{ L}^{-1}$ (geometric mean) and the total colloid surface area of 94 $\text{cm}^2 \cdot \text{L}^{-1}$ (arithmetic mean) or 210 $\text{cm}^2 \cdot \text{L}^{-1}$ (geometric mean). Because the colloids are cross-linked polynuclear species, the effective surface areas could be many times larger than the above

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} ≡ mean colloid concentration in mg · L⁻¹
 σ ≡ standard deviation
n ≡ number of samples
Peavine Canyon, Campground Spring, Whiterock Spring, and Topopah Spring are omitted due to missing data.

given numbers calculated on the basis of a hard sphere concept. Thus, with respect to the formation of actinide pseudocolloids, the colloid concentrations in groundwaters in Nevada cannot be considered as insignificant. The mean concentration of groundwater colloids on the NTS was reported to be 0.58 mg · L⁻¹ (Kingston and Whitbeck, 1991).

A very surprising and significant conclusion of the study was that a correlation between colloid concentration and sample geologic environment was not detected despite the changes in water chemistry, lithology, and varying weathering conditions of the different geologic formations (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, HCO₃, SiO₂, 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 mg · L⁻¹), Whiterock Spring (>16 mg · L⁻¹), and Beatty Well 2 (>6 mg · 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 mg · L⁻¹).

2.3 GROUNDWATER RADIACOLLOIDS 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 ⁵⁸Co, ⁶⁰Co, ⁵⁴Mn, ⁶⁵Zn 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}Th sorbed strongly to colloids in the 18- to 1,000-nm range, while only

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.

minor portions of $^{234,238}\text{U}$ are associated with particulate matter. Also at Koongarra, Seo (1990) observed groundwater colloids of kaolinite, chlorite, silica, and perhaps iron oxide, but 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 (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. (1987) 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. Vilks et al. 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 colloids are ubiquitous in all wells and springs and in all formations sampled. It is also evident that factors influencing the size, concentration, 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 to include colloid release and transport in PA calculations for the YM repository site. Although a comprehensive study has been reported on the characterization of groundwater colloids in Nevada, including one site near YM (at NTS) (Kingston and Whitbeck, 1991), very little data are available on radiocolloids. However, it is important to note that in all field studies that investigated for radionuclides (or their analogs), colloids or natural organic materials (NOM) were almost always found to be associated with radionuclides (McCarthy, 1994). 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. However, it should also be noted that the site-specific data on the existing concentration of colloids will not predict the concentration of colloids that will be present after the repository is constructed or during the post-closure period.

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. Even though NOM is composed of DOC and fixed organic carbon (FOC), a significant proportion of NOM is considered colloidal material (Figure 2-1). Dissolved organic matter is that material that passes through a 0.45- μm filter (Thurman, 1985; Choppin, 1988) and represents the bulk of the organic matter in natural systems. Much DOC consists of complex mixtures of macromolecules and aggregates that result from the degradation of plant material. Fatty and amino acids, carbohydrates, and other simple hydrocarbons include low molecular weight organic compounds, which have little capacity to sorb, or complex radionuclides. These species are smaller than the defined size for colloidal materials and are considered to be in solution.

Bacteria have a significant impact on the forms of organic matter found in groundwater. They are essential to the degradation of primary organic molecules such as cellulose. Bacteria also reproduce, and they secrete organic compounds that help in the attachment to substrates or in complexing dissolved species 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). Microorganisms are important in corrosion of metals. Oxidation of Fe often results in the formation of iron oxyhydroxide colloids. Microbes also affect the oxidation state of various metals such as uranium (Francis et al., 1991; Lovely et al., 1991).

Humic substances, the primary component of dissolved organic carbon, 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., 1987; Choppin, 1988). The humic substances are characterized by a combination of aromatic and aliphatic components (Figure 2-2). Humic and fulvic acids are macromolecules with effective diameters of 2 to 50 nm. Some humic acids have diameters as large as 110 nm (Österberg et al., 1993). Chemical composition and structural determination of the humic substances have been the subjects of many investigations (Thurman, 1985; Carlsen, 1989; Higgs et al., 1992). The reactive parts of these macromolecules consist of various functional groups such as carboxylic acids (COOH) that affect the complexing capacity as a function of the group activity.

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

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, 1985). Groundwater concentrations of DOC range from 0.05 to 0.25 $\text{mg} \cdot \text{L}^{-1}$, of which 0.03 to 0.10 $\text{mg} \cdot \text{L}^{-1}$ is humic material (Thurman, 1985).

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. Although a detailed discussion of this subject, including the types of colloids that might be generated and the

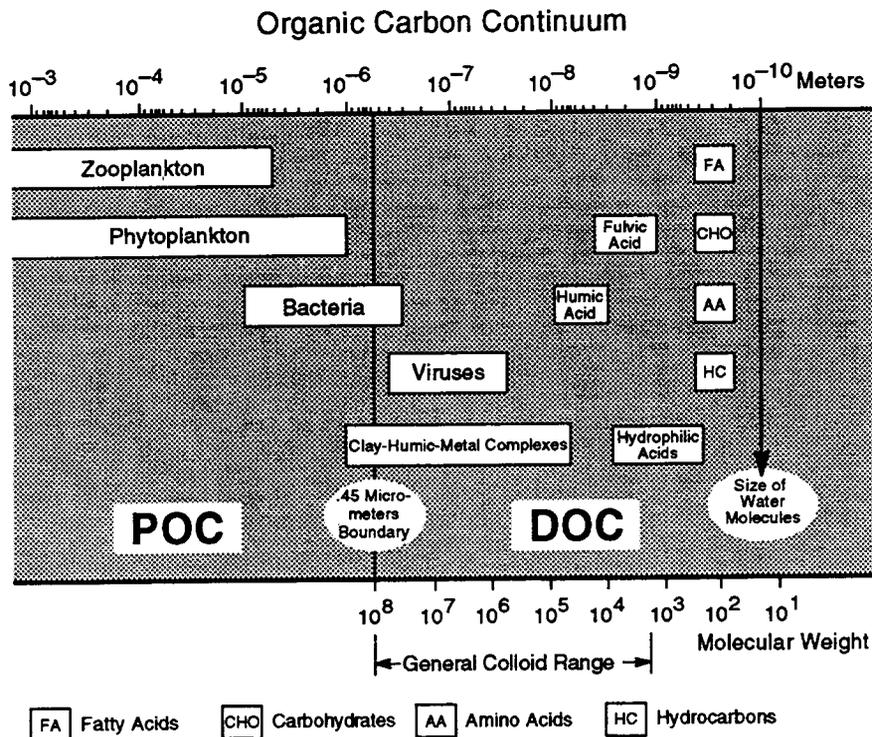
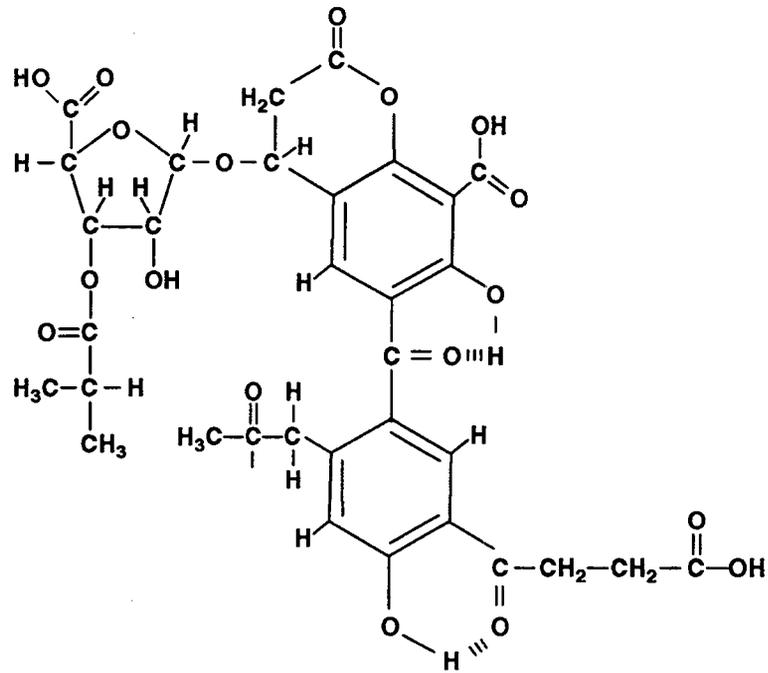


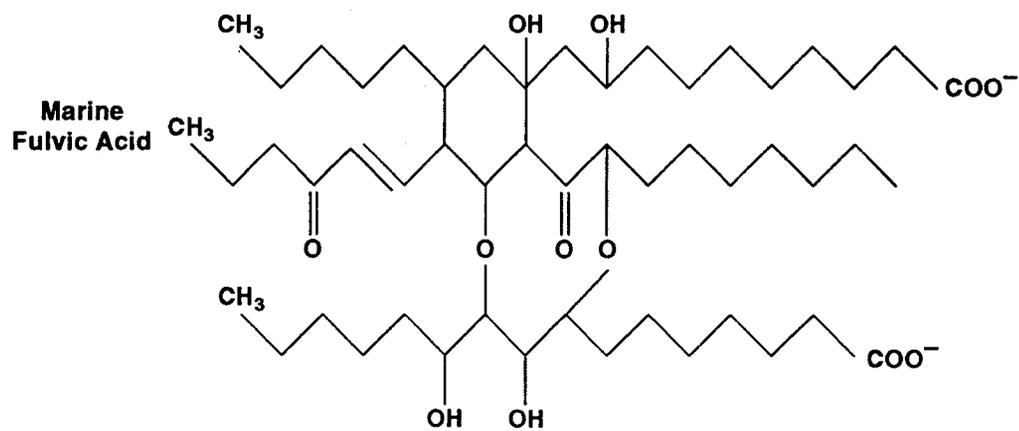
Figure 2-1. Continuum of particulate and dissolved organic carbon in natural waters (adapted from Thurman, 1985)

identification of ones that may lead to formation of transportable pseudocolloids, is not possible at this time, a recent study related to the YM site reports that 560,000 m³ of shotcrete is expected to be emplaced in repository drifts (Meike, 1993). For construction of the north exploratory shaft portal facilities, the quantity of human-introduced material 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 should 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 colloids 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 into the groundwater. Colloids formed as a result of waste package material degradation could act as substrates for sorption of radionuclides upon release of radionuclides from spent fuel and vitrified wasteform. Release of Fe ions from the waste package overpack (potentially made of carbon steel) can lead to a significant increase in the colloids in the groundwater. Such ions can accelerate the degradation rate of vitrified wasteforms. Figure 2-3 (McVay and Buckwalter, 1983) shows an example of the acceleration of borosilicate glass leaching phenomena in the presence of Fe ions in groundwaters and deionized water. Fe ions in leachant were in both dissolved and colloidal form.



(a)



(b)

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

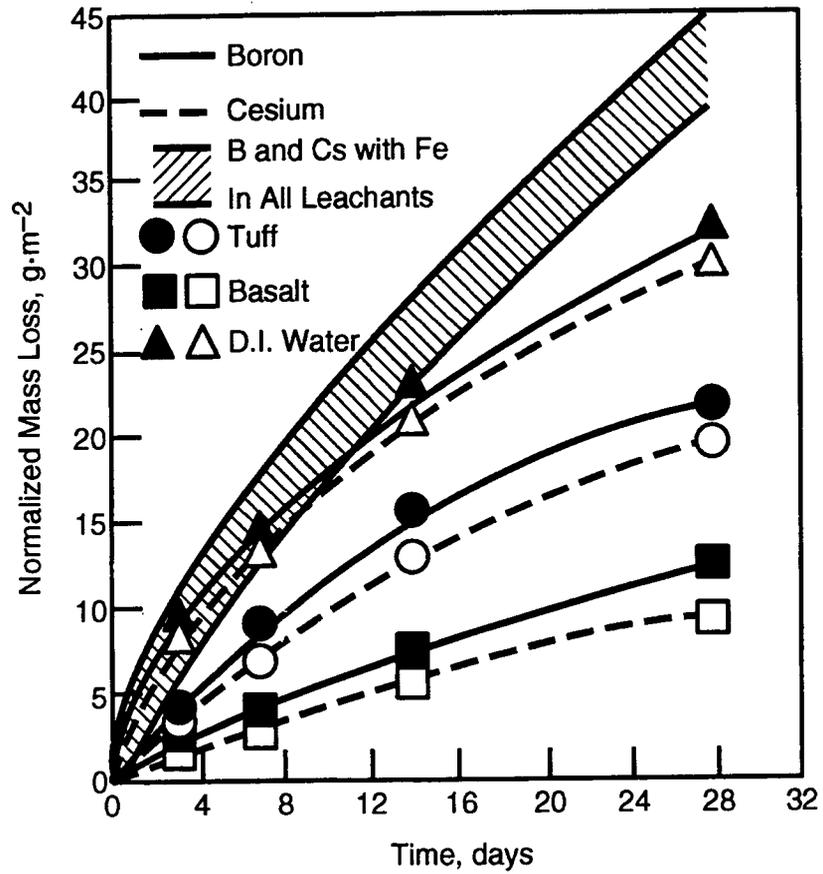


Figure 2-3. Effect of Fe in the leachant on corrosion of PNL-76-68 borosilicate glass at 90 °C with SA/V of 10 m⁻¹ (adapted from McVay and Buckwalter, 1983)

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 general mechanisms of the rates of colloid generation and growth are described. The subject of radiocolloid releases from spent fuel and vitrified wastefoms is emphasized in the context of their relevance to the YM repository site, presenting experimental data and discussing the relevant uncertainties.

3.1 COLLOIDS AND THE REPOSITORY ENVIRONMENT

The three principal sources of colloids 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 sorb or precipitate, thereby generating pseudocolloids of radioactive elements that may affect the rate of radionuclide transport from the repository to the accessible environment. These colloids are described in Sections 2 and 4.

During the initial wetting period when the thermal and radiation output of the waste is highest, degradation of 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 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 sorption of soluble radionuclides. Examples of the effects of iron are given in Section 2.5.

The current conceptual design for the proposed HLW repository at YM 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, potentially significant sources of colloids are 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 may have high solubility limits within the waters near the EBS. However, as the soluble radionuclides are transported from the EBS to the far field of the geologic repository, 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. However, as radionuclides are transported away from the EBS, the dissolved concentration is likely to decrease due to diffusion and hydrodynamic dispersion, which would reduce the likelihood of nucleation. Consideration of this aspect of radionuclide migration in a geologic environment may require detailed information, such as heat loading profiles of the waste package and the repository, 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 (Ahn, 1995; Apps et al., 1982). Condensation denotes the formation of nuclei when the groundwater becomes supersaturated with respect to a given species. The nuclei grow to 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 dispersion process arises primarily from physical or chemical weathering. Examples of physical weathering processes are freeze-thaw cycles and thermal expansion; chemical weathering includes ion exchange, heterogeneous hydrolysis, oxidation-reduction, and biological activity. In addition to nucleation and dispersion, pseudocolloids may form through the sorption of radionuclides on natural groundwater colloids or particles formed by degradation of the EBS.

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) and Ahn et al. (1993):

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

where

- R_{HN} = rate of homogeneous nucleation
 ΔG^* = free energy of nucleus formation

- k = Boltzmann's constant
- C_p = proportionality constant
- T = absolute temperature

However, homogeneous nucleation is not likely to be the principal mechanism by which colloids will form under a complex geologic environment. Therefore, modification of Eq. (3-1) is necessary.

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

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 Dispersion

Dispersion involves the breakup of solid (or condensed) material (Yariv and Cross, 1979). This process may occur during physical and chemical weathering. As vastly different mechanisms are involved in dispersion, as opposed to condensation, it is difficult to propose representative equations to describe the process applicable in a geologic environment.

3.2.3 Pseudocolloid Formation

Pseudocolloids form by radionuclides released from spent fuel sorbing onto groundwater colloids. For instantaneous reversible linear sorption, the total amount of radionuclide sorbed onto colloidal phase, S , is approximated by (Domenico and Schwartz, 1990):

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

where

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

If the sorption coefficient (K_d) is assumed to be constant, this approach is unable to explicitly account for the effects of system chemistry (e.g., pH, ionic strength) on radionuclide sorption. Another means of forming pseudocolloids, the precipitation of insoluble phases on groundwater colloids, can be interpreted as heterogeneous nucleation.

3.2.4 Growth

Once formed, radiocolloids may change in size. Colloids 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. 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:

$$\frac{dm}{dt} = \frac{DA_c}{\delta + \frac{D}{k_r}} (C - C_s) \quad (3-4)$$

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. (3-4) can be reduced to:

$$\frac{da}{dt} = G = k_G S \quad (3-5)$$

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 (3-5) 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. (3-5), such as:

$$G = G_0(1 + ma)^n \quad (3-6)$$

where

G_0	=	growth rate for $a = 0$
m, n	=	adjustable parameters

Small particles also grow through flocculation. The flocculation process is described in Section 5.4.1.

3.2.5 Influence of Temperature on Formation and Growth

The expressions in Eqs. (3-1), (3-3), (3-4), and (3-5) demonstrate that colloid formation 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 formation 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.

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 of water 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 (Ahn, 1994), 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 solubility, aqueous chemistry, and 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 $(^{239+240}\text{Pu}, ^{241}\text{Am}, \text{ and } ^{244}\text{Cm})$ in immersion tests at 85 °C. The first cycle shown in the figure used as-received bare spent fuel. 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 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). ^{241}Am and ^{244}Cm colloids were more pronounced in later cycles. 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 °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.

Nucleation Processes

Despite the difficulties in distinguishing among colloids formed by the different mechanisms, nucleation and condensation may form colloids from spent fuel under conditions anticipated in a geologic repository (Ahn, 1995). 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

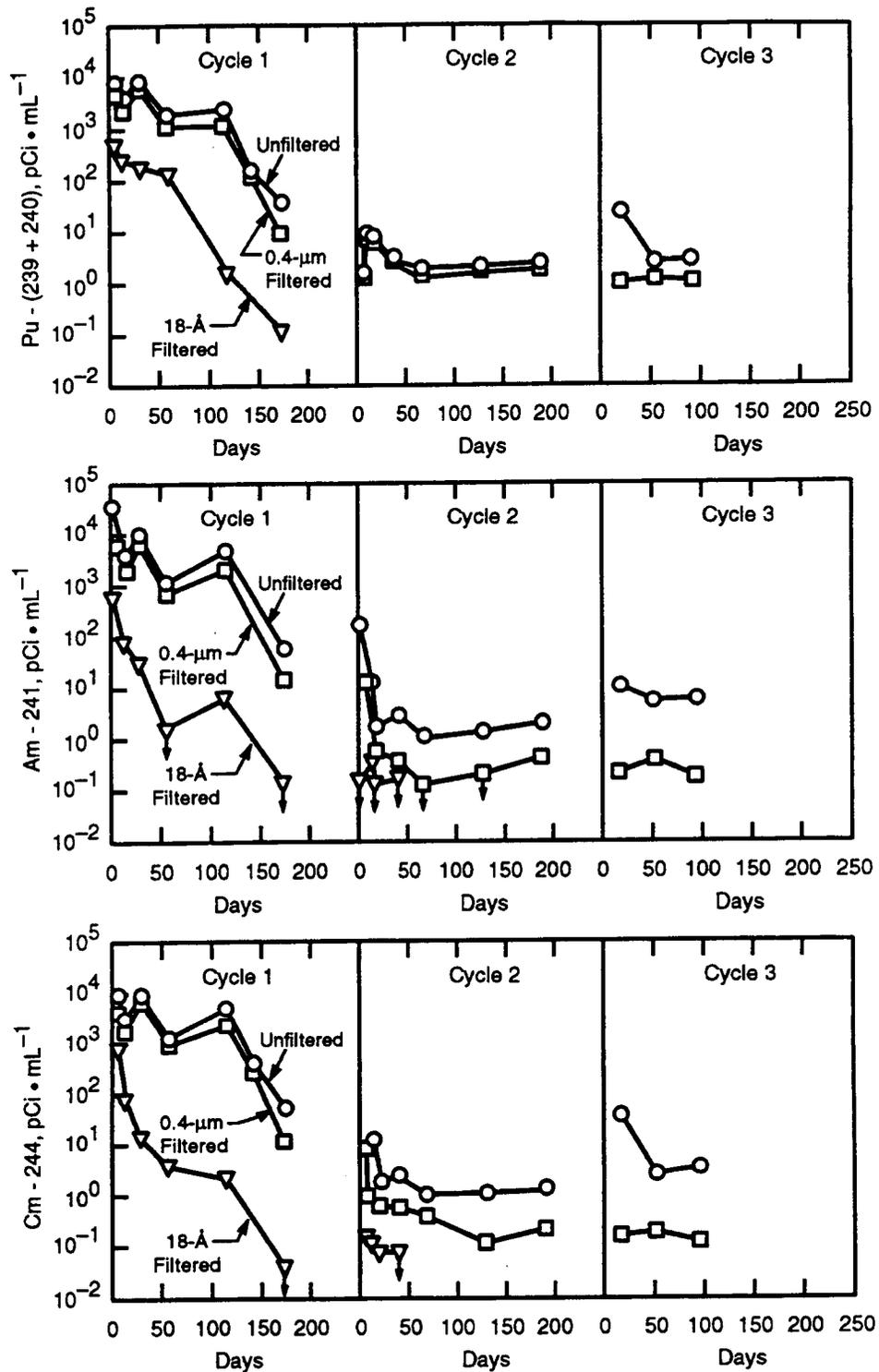


Figure 3-1. Effects of filtration on release of radionuclides from bare spent fuel at 85 °C in J-13 groundwater (adapted from Wilson, 1990b). (The small arrows indicate that the analyses are below detection level.)

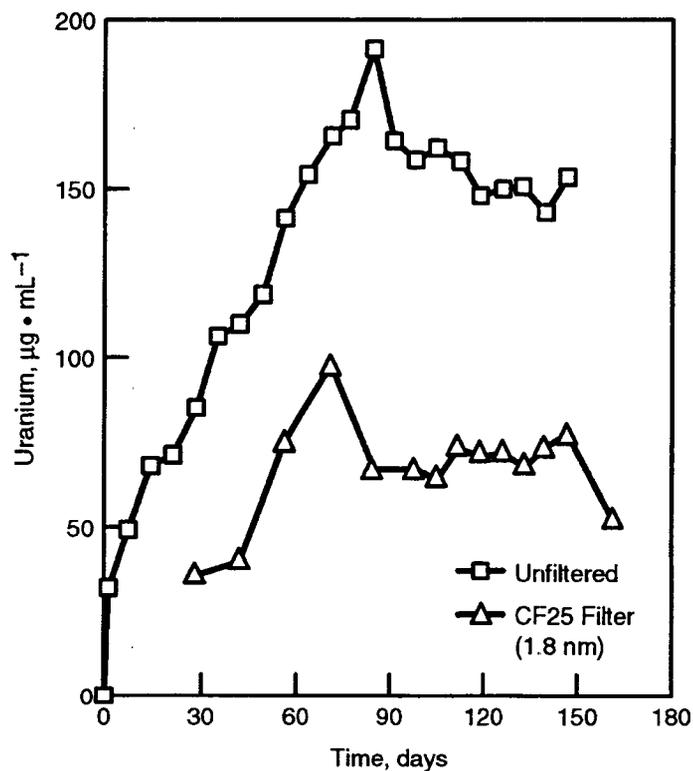
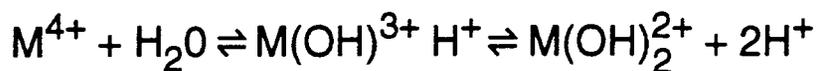


Figure 3-2. Filtering effects on the uranium concentrations in the dissolution of polycrystalline UO_2 in J-13 groundwater at room temperature (adapted from Veleckis and Ho, 1991)

Hydrolysis



Condensation

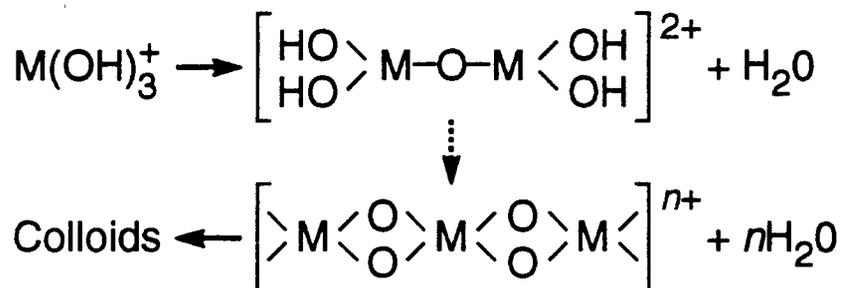


Figure 3-3. Hydrolysis and condensation processes for colloid formation (adapted from Maiti et al., 1989)

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 colloid geometries involved makes calculation of heterogeneous nucleation rates much less straightforward. Therefore, PA calculations may be dependent on estimates using homogeneous nucleation rates modified by a shape factor.

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, Fe or Si colloids, or simultaneous formation of more than one phase. Experimental data on these complicating factors are not available for developing more sophisticated models.

Nucleation of colloidal material should decrease as the altered layer develops and dissolution of spent fuel is inhibited. However, further dissolution may occur, resulting in the formation of more colloids if (i) the altered layer becomes unprotective, is disrupted, or removed; and (ii) leachate is replenished or colloids are removed. 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.

Dispersion Processes

The dispersion process in waste form degradation may involve spallation from the spent fuel surface, detachment of grains, or disintegration of grains or particles (Ahn, 1995). 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 4.4.1.2. The second type of disintegration results from preferential dissolution of grain boundaries (Wronkiewicz et al., 1992). The third type of disintegration results from internal 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. For example, spallation of UO_2 occurs during oxidation of spent fuel at temperatures over 250 °C (Einziger et al., 1992). The spallation is likely due to the large volume change (~35.8 percent) that occurs during the transformation from UO_2 to U_3O_8 .

As an example, 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 that may reduce the accumulated strain energy.

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 also may 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.

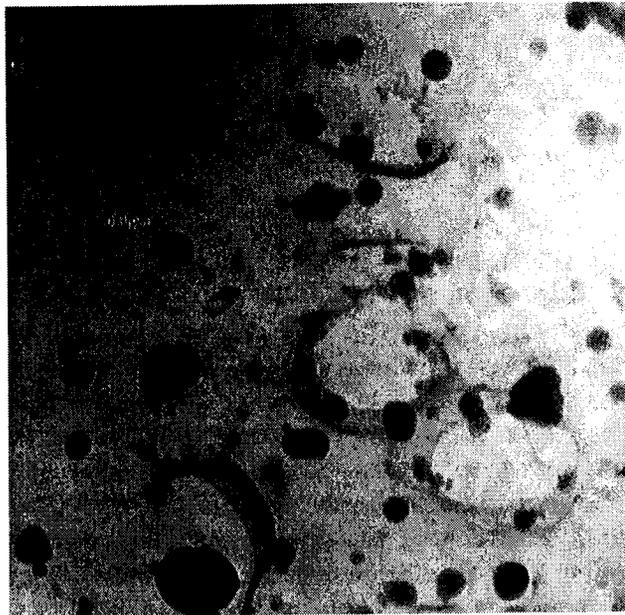
Sorption Processes and Pseudocolloid Formation

In addition to condensation or dispersion processes, pseudocolloids also may form by sorption of ions on natural groundwater colloids corrosion products from EBS materials. Groundwater in the vicinity of YM 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 μm (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 YM site (U.S. Department of Energy, 1988). The presence of naturally occurring groundwater colloids supports the possibility of forming pseudocolloids. In addition, it should be noted that concentration of existing colloids (both organic and inorganic) is likely to be affected by the repository construction and the introduction of materials such as iron in waste packages and cement in shaft and drift sealing materials.

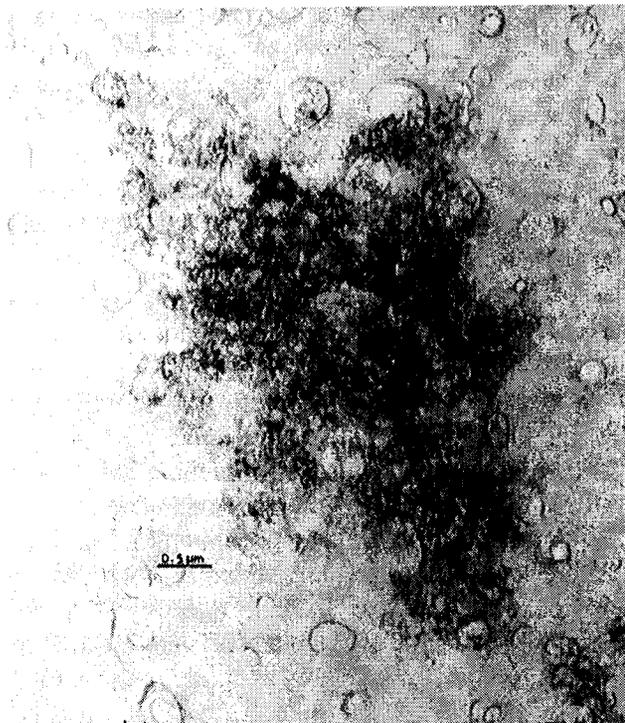
3.3.2 Vitrified (Glass) Wasteforms

Most of the general discussion in Section 3.3.1 about spent fuel dissolution is also relevant to vitrified (glass) wasteform leaching. The detailed 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 due to differences in the buffering capacities of the two wasteforms. 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 (Ahn et al., 1993). The processes of colloid formation, described earlier for spent fuel, have been reported in literature for vitrified wasteforms (Ebert et al., 1993; 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).

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



(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 liquid spalled from the glass surface (Bates et al., 1992c)

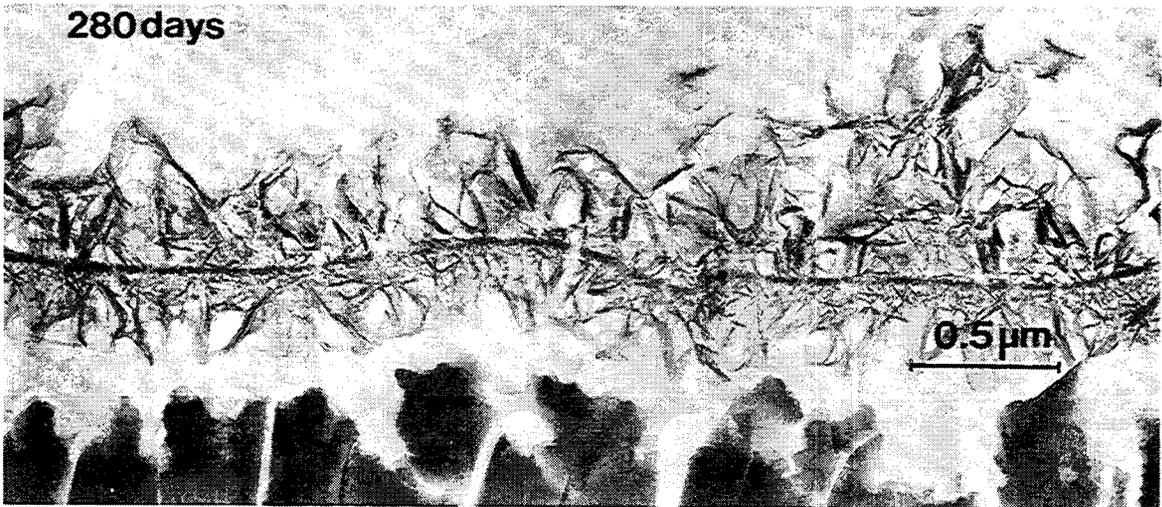
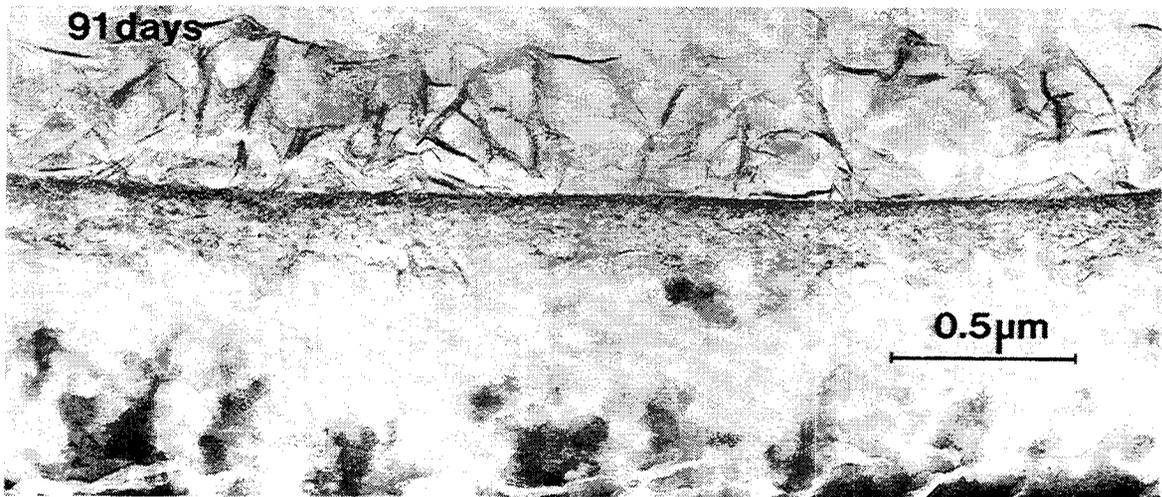
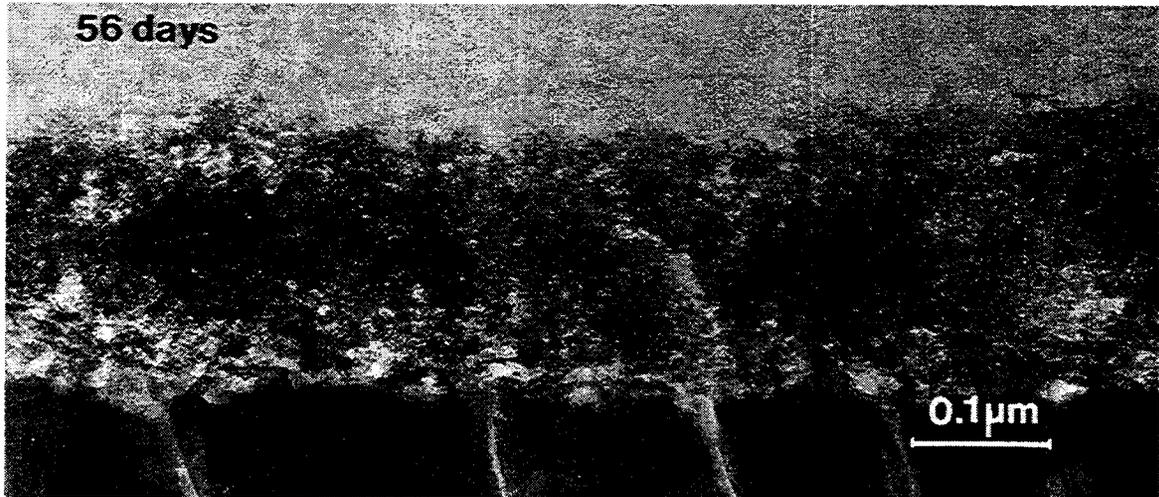


Figure 3-5. Brightfield electron micrographs of cross sections of glass reacted for (a) 56 d, (b) 91 d, and (c) 278 d, showing the formation of smectites (Bates et al., 1992c)

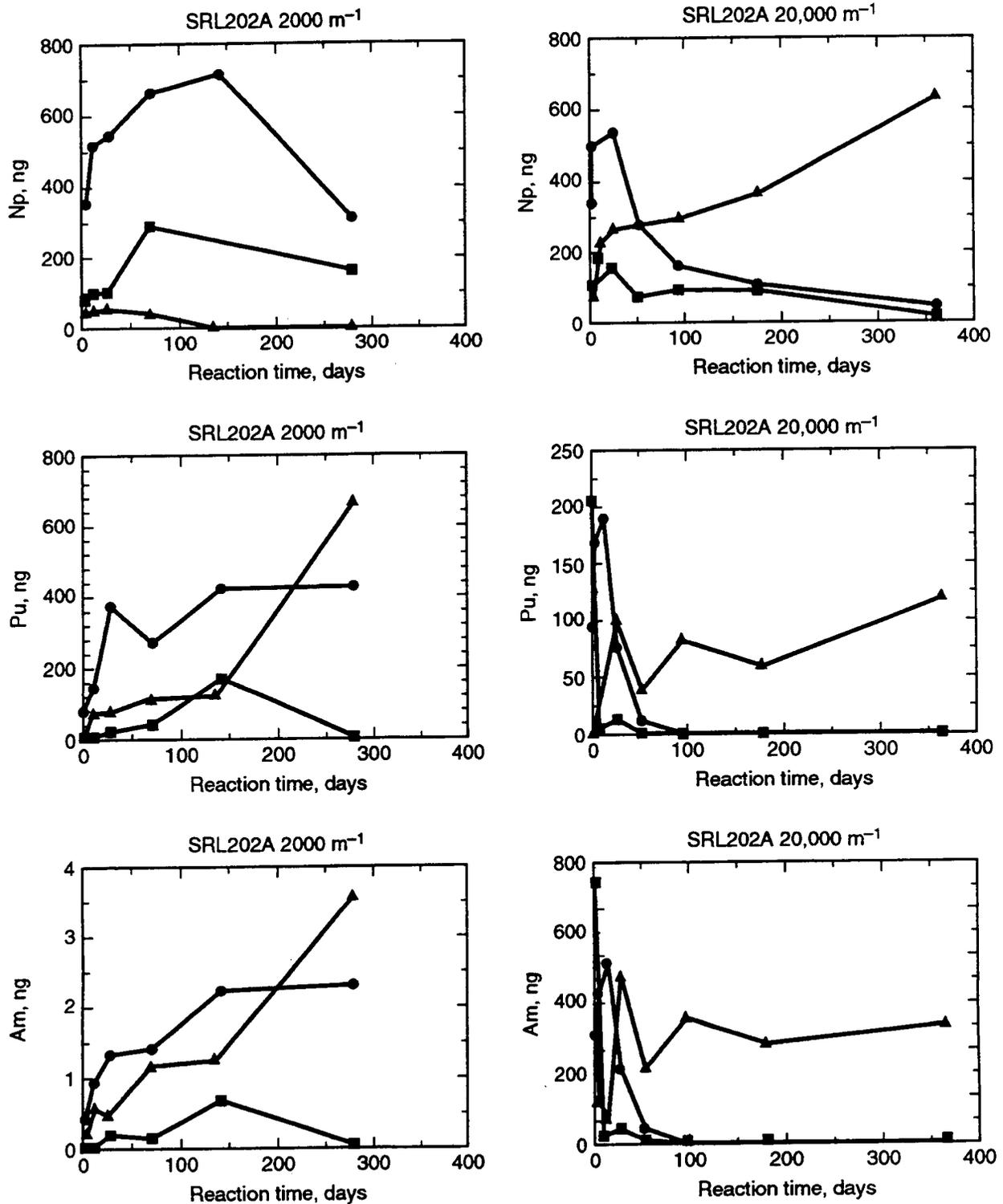


Figure 3-6. Mass action in (•) 0.45-µm filtrate, (■) 60-Å filtrate, and (▲) acid soak solution for tests with SRL 202A glass at SA/V=2,000 m⁻¹ (20 cm⁻¹) and SA/V=20,000 m⁻¹ (200 cm⁻¹) in equilibrated J-13 groundwater at 90 °C (Ebert and Bates, 1992)

Bates, 1992), actinide release is reported at two different values of specimen surface area (SA) to leachate volume (V) ratios. Mass action in (•) 0.45- μm filtrate, (■) 60- \AA filtrate, and (▲) acid soak solution is shown in the figure. 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 μm) decrease as time increases. This decrease is attributed to high pH and ionic strength. At the lower SA/V of $2,000 \text{ m}^{-1}$ (20 cm^{-1}), pH is lower than at the higher SA/V ratio, and colloids appear to be stable. In this work, particles greater than 0.45 μm were not included in the analysis. These big particles attenuated the alpha spectra.

Shade and Strachan (1986) used MCC-3 tests (immersion with slow agitation) using crushed simulated (nonradioactive) vitrified wastefrom in deionized water and silica water at 90 °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, 1992). Under drip test conditions of J-13 well water at 90 °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 °C (adapted from Bates et al., 1992b)

Fraction	Np		Pu + Am	
	#1	#2	#1	#2
	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 wastefrom has been suggested as a principal factor in colloid release because the silica (SiO_2) matrix is the main constituent of the wastefrom (Avogadro and de Marsily, 1984). Experimental evidence (Ebert and Bates, 1992) suggests that the flocculation or the growth of colloids occurs only at large values of surface area to volume ratio (SA/V), high ionic strength, or at high pH in static immersion tests. It is uncertain if the colloid material formed during glass alteration will be removed from the wastefrom surface by advection or will settle out under repository conditions.

3.3.3 Growth and Stability of Colloidal Suspension

The mechanisms of colloid formation during waste form degradation have been discussed, in general, earlier in the report. However, it is difficult to clarify details of the growth stage because there are not enough available data on this subject. It is believed that colloid stability follows the general rules discussed in Sections 4.4.2 and 5.2. An example of such colloid stability is colloid formation during glass leaching, discussed in 3.3.2. Detailed information is also not available on this subject.

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 geologic setting and geochemical features of the YM potential 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 volcanic rocks in the vicinity of YM 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. 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 (Cornwall, 1972; 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 Crater Flat, Calico Hills, and Paintbrush Tuffs (Figure 4-1), and the Timber Mountain Tuff, which overlies them on the eastern flank of YM. Tertiary units at YM decrease in thickness from west to east.

Precambrian metamorphics and Paleozoic carbonate rocks do not crop out in the exploratory block, but they are believed to underlie the Tertiary volcanics of YM (U.S. Department of Energy, 1988; Mattson et al., 1989; McKague et al., 1989). To date, however, a drill core along the mountain crest (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 drill hole UE-25p#1 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 YM 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 YM (U.S. Department of Energy, 1988). The YM structural block itself has been tilted to the east along a series of north-trending high-angle Basin and Range normal faults such as the Solitario Canyon fault (Figure 4-2).

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 YM 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 YM 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 YM 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 YM. The amount of suspended matter is generally small, on the order of 1 to 10^{-2} mg \cdot 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). Fracture apertures at YM, 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 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 μ m. 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

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)
Tuffaceous Beds of Calico Hills		Calico Hills Non-Welded Unit (CHn)
Crater Flat Tuff	Prow Pass Member	Zeolitized (CHnz)
	Bullfrog Member	
		Crater Flat Unit (CFu)

Note: Figure Not to Scale

Figure 4-1. Tertiary stratigraphy and hydrostratigraphic units in the Yucca Mountain exploratory block. The repository horizon is the Topopah Spring Member. The diagonal line represents the separation between the vitric and zeolitized tuffs and approximates the location of the static water level (adapted from U.S. Department of Energy, 1988)

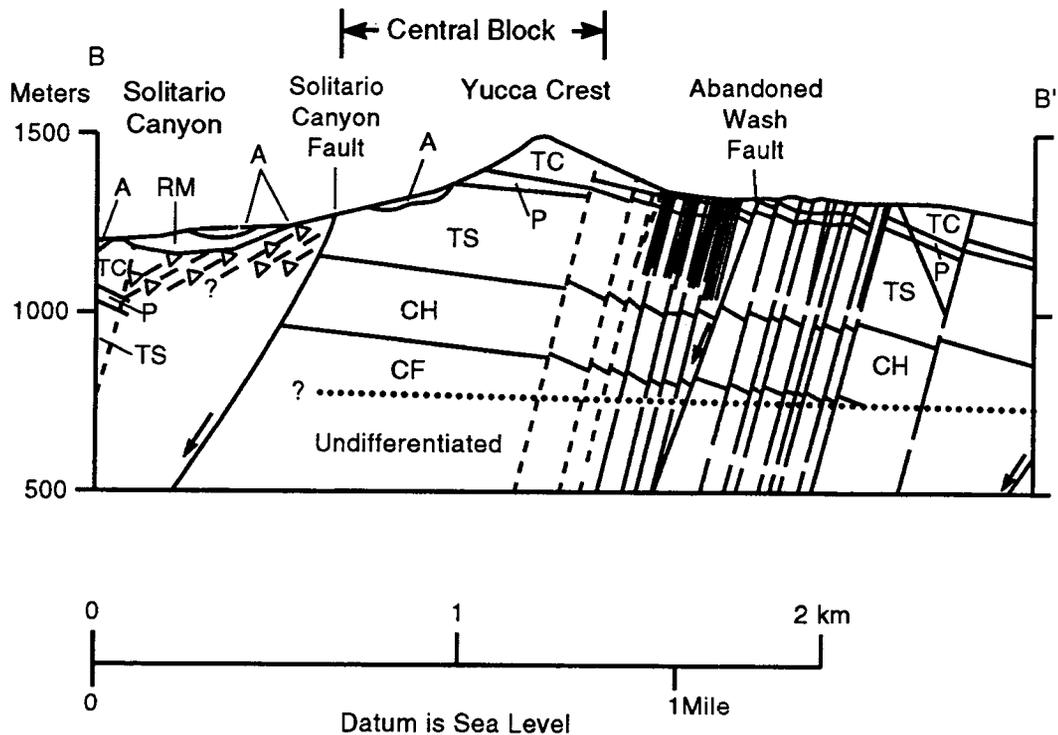


Figure 4-2. East-west cross section of Yucca Mountain looking to the north. The horizontal dotted line shows the approximate location of the static water level. Unit symbols are: A—Alluvium; RM—Rainier Mesa member of the Timber Mountain Tuff; TC—Tiva Canyon Welded Unit; P—Paintbrush Nonwelded Unit; TS—Topopah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

4.5 mg·L⁻¹. Although this concentration is higher than the J-13 waters (10⁻³ to 10⁻⁵ g·L⁻¹), Buddemeier and Hunt (1988) report relatively high pumping rates (~120 L·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) mg·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.

Well J-13 in Jackass Flat to the east of YM 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 scanning electron microscopy (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 YM. 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 Formation of Real or True Colloids

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). For example, laboratory studies by Olofsson 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 suspension. Both Am and Pu exhibited appreciable colloidal formation with increasing 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). Depending on the oxidation state of the actinide of interest, however, true colloids may form over a wide range in pH. This is especially true for actinides in the +4 oxidation state. Kim et al. (1987) 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. 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 at YM is not understood completely, however, the relatively dilute conditions (ionic strength≈10⁻³ molal for Well J-13) should not inhibit hydrolysis and should favor colloidal stability of hydrolysis and polymerization products.

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±0.05 mg·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 meq·g⁻¹ for the fulvic acid fraction of TOC, and 4.6 meq·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 YM 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 colloids factored into radionuclide transport calculations. One approach to modeling pseudocolloid migration is 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, however, does 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 presents a brief summary of the surface characteristics of a variety of the more common colloidal material found in a natural groundwater system and describes the potential for sorption of radionuclides on a colloid phase during transport in a geologic environment.

4.4.1.1 Sorption on Groundwater Colloids—Inorganics

Potential inorganic colloids in a groundwater system include oxides and oxyhydroxides, clays, and micas, silicates and aluminosilicates, and carbonates. The availability of natural (or human-introduced particles) for radionuclide transport in suspension is affected by 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 in the pore water. 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 autogrinding between suspended particles.

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 and NOM on oxides 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 metal (Me) (hydr)oxide-water interface is composed of amphoteric surface hydroxyl ($\equiv\text{MeOH}^0$) 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 ($\equiv\text{MeOH}_2^+$ sites are dominant). As pH increases, H^+ activity is low, and deprotonated sites (i.e., $\equiv\text{MeO}^-$) 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 $\equiv\text{MeOH}_2^+$ sites, while cations will be adsorbed at deprotonated $\equiv\text{MeO}^-$ sites. This process leads to the formation of a sharp sorption edge where sorption of cations increases (as the number of $\equiv\text{MeO}^-$ sites increases) from 0 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 (Balistreri 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; Venkataramani 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, at the low end of the range (~ 4 to ~ 9) reported in the vicinity of YM (U.S. Department of Energy, 1988). Limited experimental data (Hsi, 1981) suggest that cation competition with common groundwater ions such as Ca^{2+} and Mg^{2+} 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., 1994; Righetto et al., 1988, 1991) and TiO_2 (Lieser and Thybusch, 1988; Venkataramani and Gupta, 1991) exhibits a similar behavior. This dependence of sorption behavior on total carbon concentration is relevant to conditions at YM 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).

Clays and Micas

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 earlier for oxides and oxyhydroxides. Some clays, such as 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

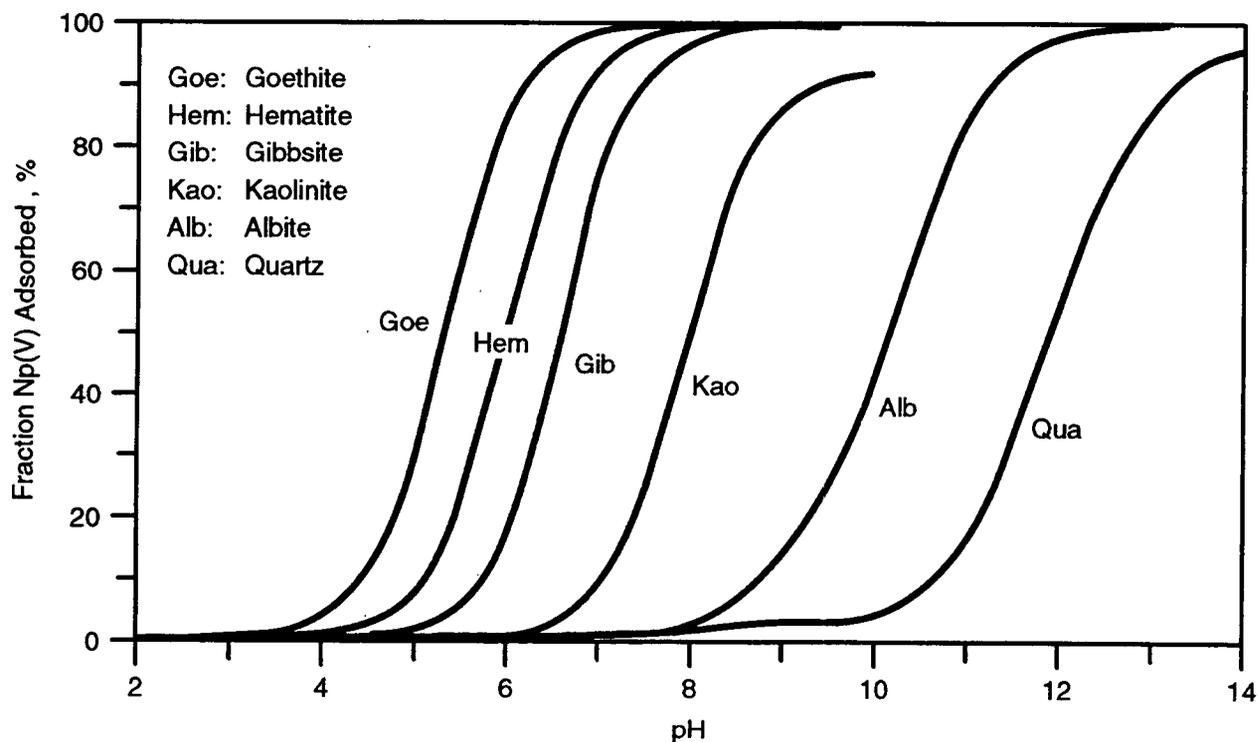


Figure 4-3. Predicted adsorption of Np(V) as a function of pH onto different minerals ($Np_T = 1.1-1.3 \times 10^{-7}$ M). A triple-layer surface complexation model (Davis and Kent, 1990) was used assuming a total site concentration for each mineral of 5×10^{-4} M (adapted from Kohler et al., 1992).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

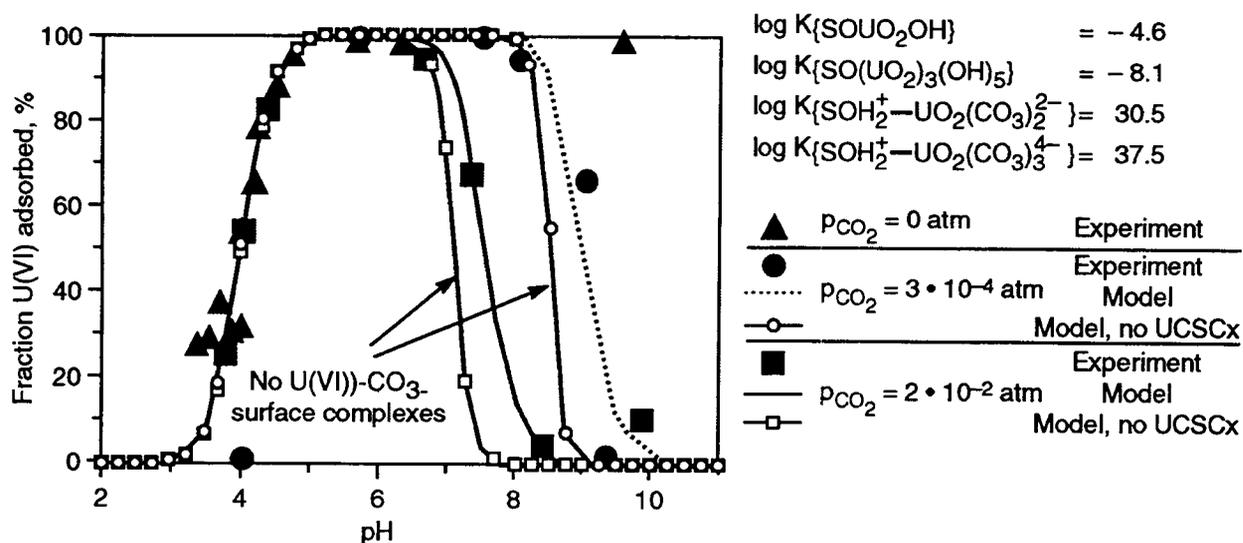


Figure 4-4. Uranium sorption on goethite ($U_T = 10^{-6}$ M). Model predictions using a triple-layer surface complexation model (Davis and Kent, 1990) (adapted from Kohler et al., 1992).

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. Comans et al. (1991) suggest that this higher rate of Cs^+ sorption is 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 micas. This behavior suggests that sorption of these radioelements is controlled by the edge sites.

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

Silicates and aluminosilicates 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 surfaces can be treated as a combination of site types (e.g., $\equiv\text{AlOH}^\ominus$ and $\equiv\text{SiOH}^\ominus$), 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 interlayer 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 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). Recent studies (Righetto et al., 1991; Moulin et al., 1992) of the adsorption of Am^{3+} , NpO_2^+ , and Th^{4+} on amorphous silica colloids have observed a dependence of radionuclide sorption on both pH and radioelement oxidation state.

Carbonates

In carbonate aquifers, calcite and dolomite are reported as colloids and suspended particles. The presence of Paleozoic carbonates and secondary calcite mineralization in the vicinity of YM suggests a potential role for these minerals in radionuclide transport. 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 $\text{p}(\text{CO}_2)$. 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), but no data are available yet for radionuclide sorption on carbonates.

4.4.1.2 Sorption on Groundwater Colloids—Organics

The sorption of radionuclides onto microbes or humic colloids involves complexation with available functional (acidic) groups. This complexation is a function of pH, oxidation state of species, and composition of water (including ionic strength). This complexation process can 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. Sorption of

organic colloidal material on silicate and oxide mineral surfaces affects the sorption capacity of those phases that, in turn, will impact the uptake of radionuclides. 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 on the order of 10^{-6} M, however, have only a slight effect on the sorption behavior (Figure 4-5).

Microorganisms

A variety of microorganisms may be found in the subsurface geologic media (Phelps et al., 1989). In addition to affecting biodegradation, these organisms may affect transport of radionuclides in the following ways:

- (i) Binding the metal species to the surface of the cell
- (ii) Transforming the metal species to another by redox reactions such as 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. The tendency to form complexes will decrease with increased concentration of metal species on the surface (Xue et al., 1988).

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.

Humic Substances

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). 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:



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 (Higgs 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)

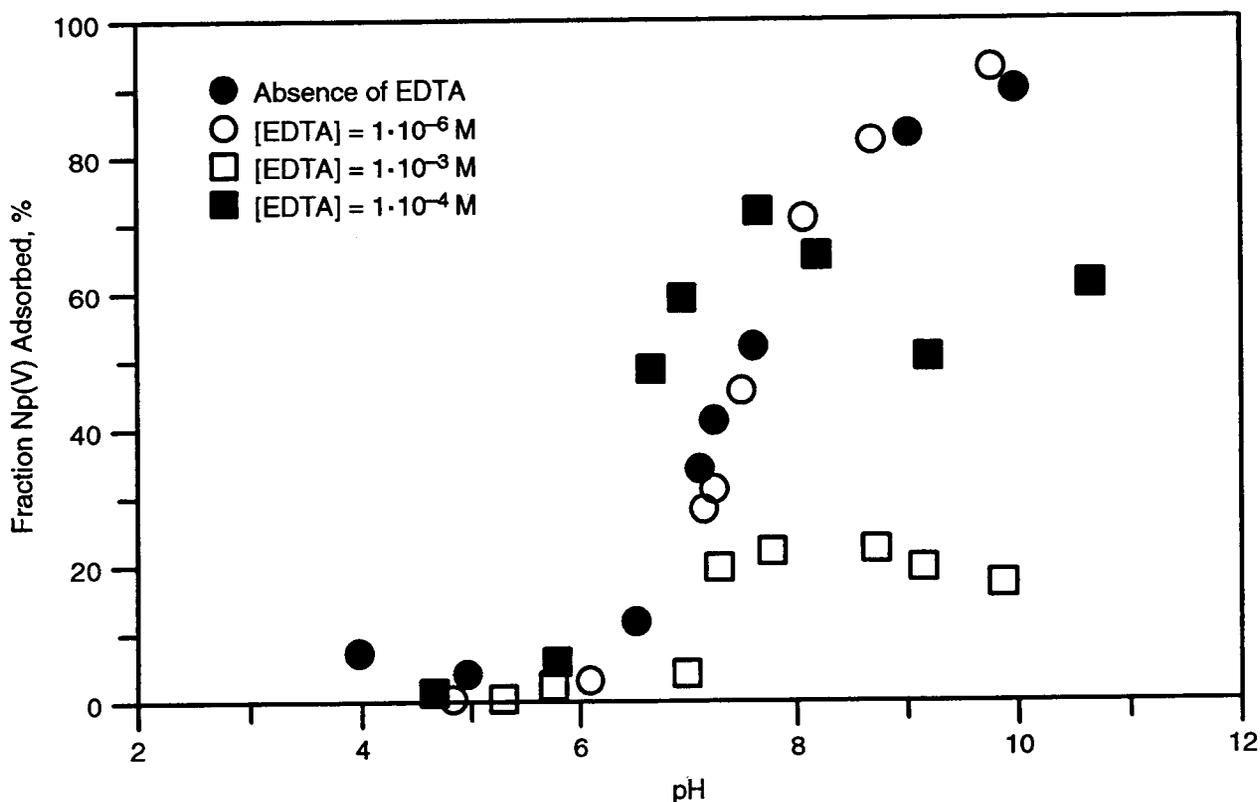


Figure 4-5. Np(V) sorption on kaolinite in the presence of different concentrations of ethylenediaminetetraacetic acid (EDTA). $Np_T = 1.2-1.3 \times 10^{-7}$ M (adapted from Kohler et al., 1992).

- (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). True colloids 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, 1985). Numerous investigations of organic-mineral and organic-metal-mineral complexes have been conducted to establish the partitioning of metals in natural waters (Thurman, 1985; Carlsen, 1989; Stumm, 1992). Sorption of organic matter on minerals such as $\gamma-Al_2O_3$, silica, or iron oxyhydroxides (goethite, hematite) is a function of pH (Krummert and Stumm, 1980). The coating of mineral surfaces with organic matter may affect the surface charge and thus affect colloidal stability and sorption of radionuclides (Bidoglio et al., 1989).

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 pH and

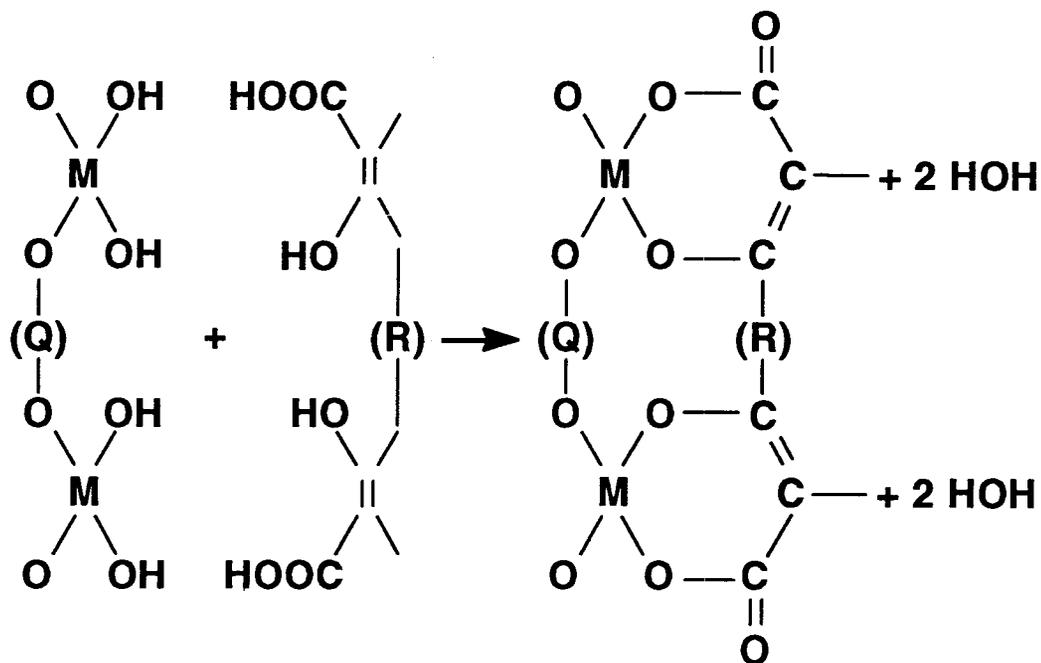


Figure 4-6. Dehydration mechanism for sorption of radiocolloid on humic colloid

humic acid concentration. At high pH, the humic acids form complexes with Am(III), 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

4.4.2.1 Inorganic Colloid Transport

If actinides and other radioelements can sorb onto natural groundwater colloids or form true colloids, the stability of the particles in suspension is of critical importance in colloid-mediated transport. Stability of metal-oxyhydroxide particles 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). Under certain chemical conditions, the presence of ligands such as HCO_3^- and SO_4^{2-} can also affect the formation of oxides by consuming metal ions in the precipitation of carbonate or sulfate solids. Also, as discussed earlier, the sorption 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 from colloid particles, they are free to sorb onto an immobile medium that might have a stronger affinity for a given radioelement.

In addition to pH controls on the sorption 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 Na^+ , the EDL around charged particles extends further into the solution (Hunter, 1987) at lower ionic strength. This phenomenon can cause the expansion of swelling clays, and also tends to promote dispersion of charged particles and stabilization of colloid suspensions. 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).

In granitic waters in Switzerland, Degueldre (1993) 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. The correlation between Ca^{2+} and particle concentration is not perfect, however, and this interpretation is uncertain due to other components of the different groundwaters that may contribute to colloid formation. Variations in pH also affect particle stability. At low pH, the variable surface charge of many minerals 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 occurs, and the suspension is destabilized. As the pH increases towards the oxide 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 and organic material, dispersion is enhanced, and the clay and organic colloids are kept in suspension (Suarez et al., 1984).

Most studies of colloid stability and transport have been limited to hydrologically saturated conditions. To help evaluate colloid transport through the vadose zone, 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 due to capillary forces, while decreasing ionic strength or increased flow rate will lead to desorption at the glass-water interface. Based on the experimental results, Wan and Wilson (1994) 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. In field studies, Read and Hooker (1989) proposed transport and strain filtering of Th associated 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 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.

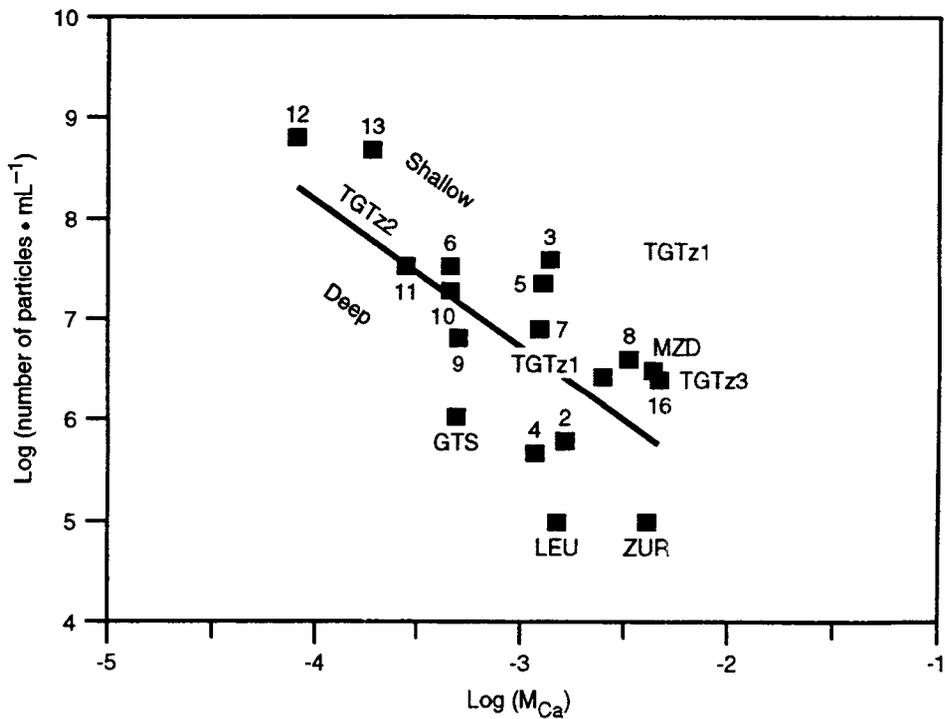
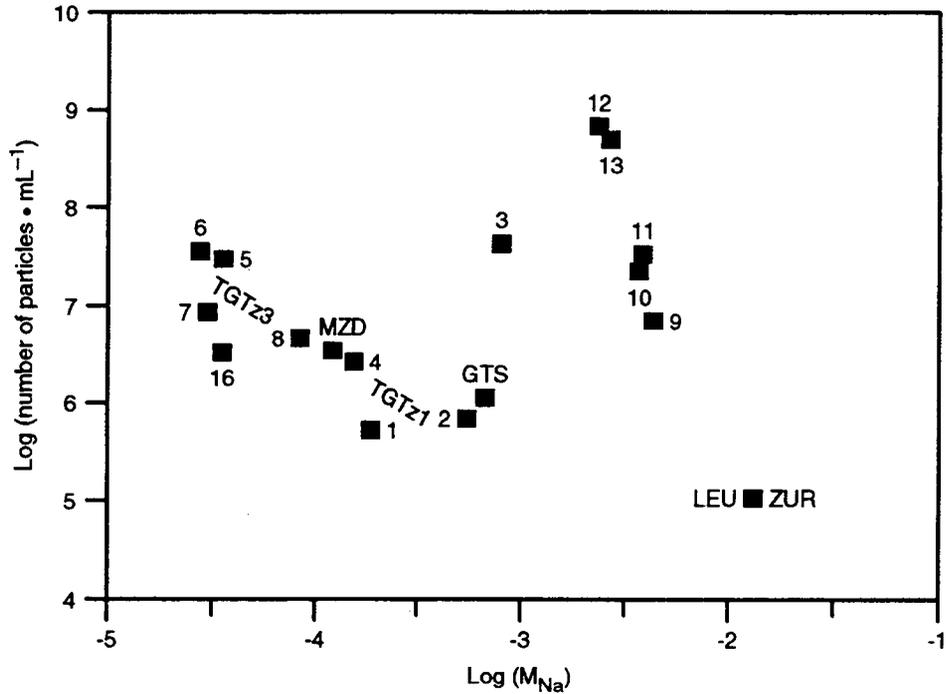


Figure 4-7. For granitic groundwaters collected from Switzerland: (a) colloid (>100 nm) concentration versus Na⁺ concentrations (molarity), (b) colloid (>100 nm) concentration versus Ca²⁺ concentration (molarity). TGT—Transitgas Tunnel (Zones 1, 2, 3), MZD—Menzenschwand, LEU—Leuggern, ZUR—Zurach, GTS—Grimsel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

4.4.2.2 Organic Colloid Transport

Transport of organic colloidal material and biocolloids is subject to many of the same constraints that affect transport of inorganic colloids, such as surface charge, size, and ionic strength. Organic colloids may even be transported as sorbed phases on clays or iron oxyhydroxide whereas microbes may attach to other substances with *pili* (filaments) or a mucilage excrement.

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 μm and the viruses were only 0.023 μm 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. Similar to Wan and Wilson's (1994) observations, 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 affecting the coagulation and subsequent flocculation of colloidal material. At low concentrations, 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 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 sorption, binding of radionuclides by microorganisms, and radionuclide 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. It is anticipated that much of the organic material present in the post-closure repository will be due to human-introduced materials such as oils, lubricants, and polymeric materials. 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

Colloids have been observed in the saturated groundwaters of the YM 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

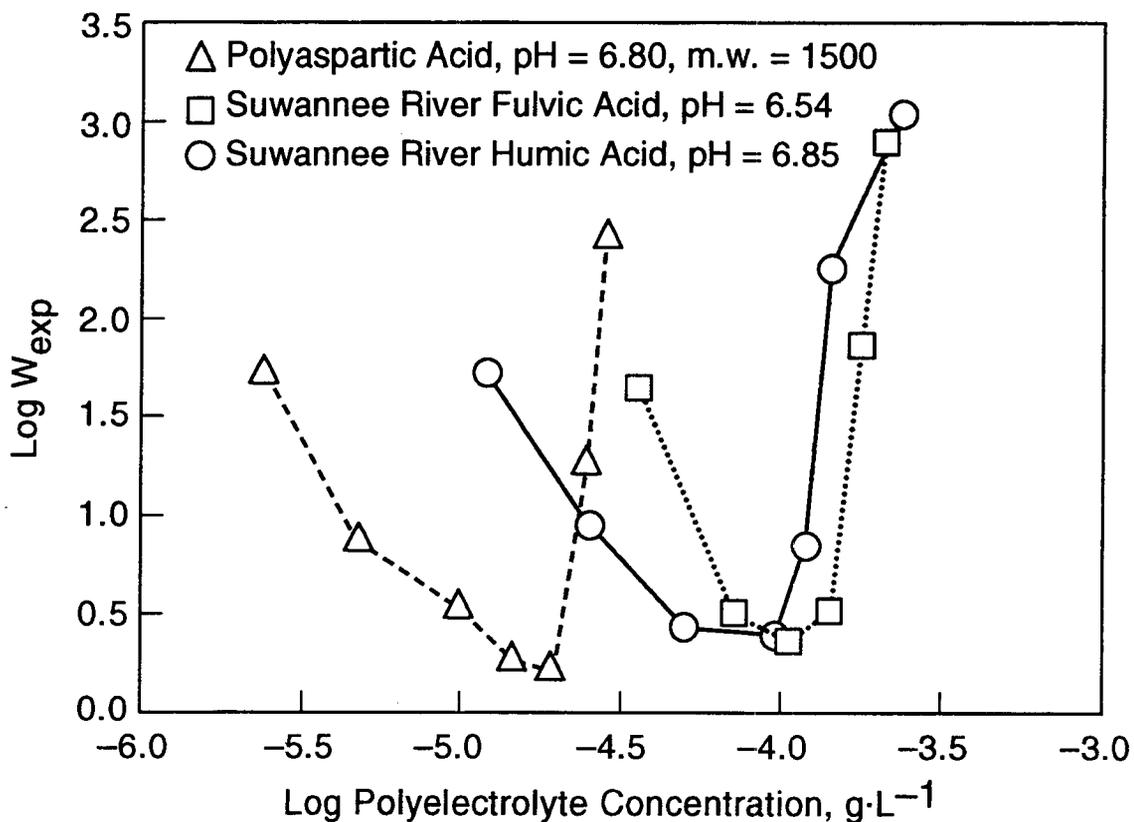


Figure 4-8. Experimentally derived stability ratio, W_{exp} , of a hematite suspension, plotted as a function of polyelectrolyte concentration in the presence of 1 millimolar NaCl. Hematite concentration is $17.2 \text{ mg}\cdot\text{L}^{-1}$ (adapted from Liang and Morgan, 1990).

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 YM. 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).

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 YM 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 YM environment, the extent to which they could contribute to overall radionuclide transport remains unclear. If the concentration of colloids in the unsaturated (and saturated) zone is small, 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 PA.

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 1.5 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. Limitations of existing models regarding colloid transport under the aforementioned conditions are identified. 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 modeling at HLW disposal sites has occurred 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), van der Lee et al. (1993), Grinrod and Cooper (1993), and Vilks (1994), among others. 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 disposal, 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 (McCarthy and Zachara, 1989; McCarthy and Degueudre, 1993). 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 Inherent Instability

An important distinction between colloid suspension and solutions is stability. The stability of a colloidal suspension is an important property for, to a large extent, it will 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.

5.2.1.1 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.

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. *Surface and Colloid Science*. Summer Short Course. Seattle, WA: University of Washington.

5.2.1.2 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 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.

5.2.1.3 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.

5.2.2 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. Common shapes of aqueous colloids include rod, lath or ribbon, thread, disk, sphere, plate, prolate, and oblate. 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 geometrical shapes as described above.

The mean colloid diameter, \bar{d}

$$\bar{d} = \frac{\sum n_i d_i}{\sum n_i} \quad (5-1)$$

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

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

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

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

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 5-1). 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 YM 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

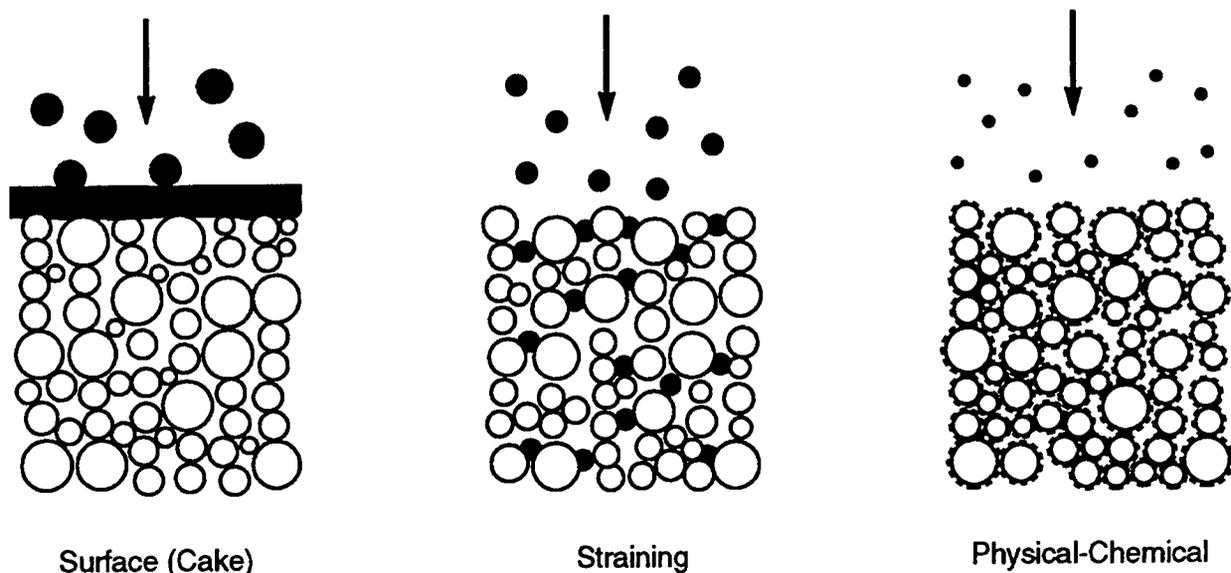


Figure 5-1. Mechanisms for colloid straining in porous media (adapted from McDowell-Boyer et al., 1986)

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 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 YM 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 move 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 5-2. 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 earlier. 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) (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 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 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 or electrostatic repulsion, colloids most likely will not experience the minimum water velocity, and, consequently, the average colloid velocity may be

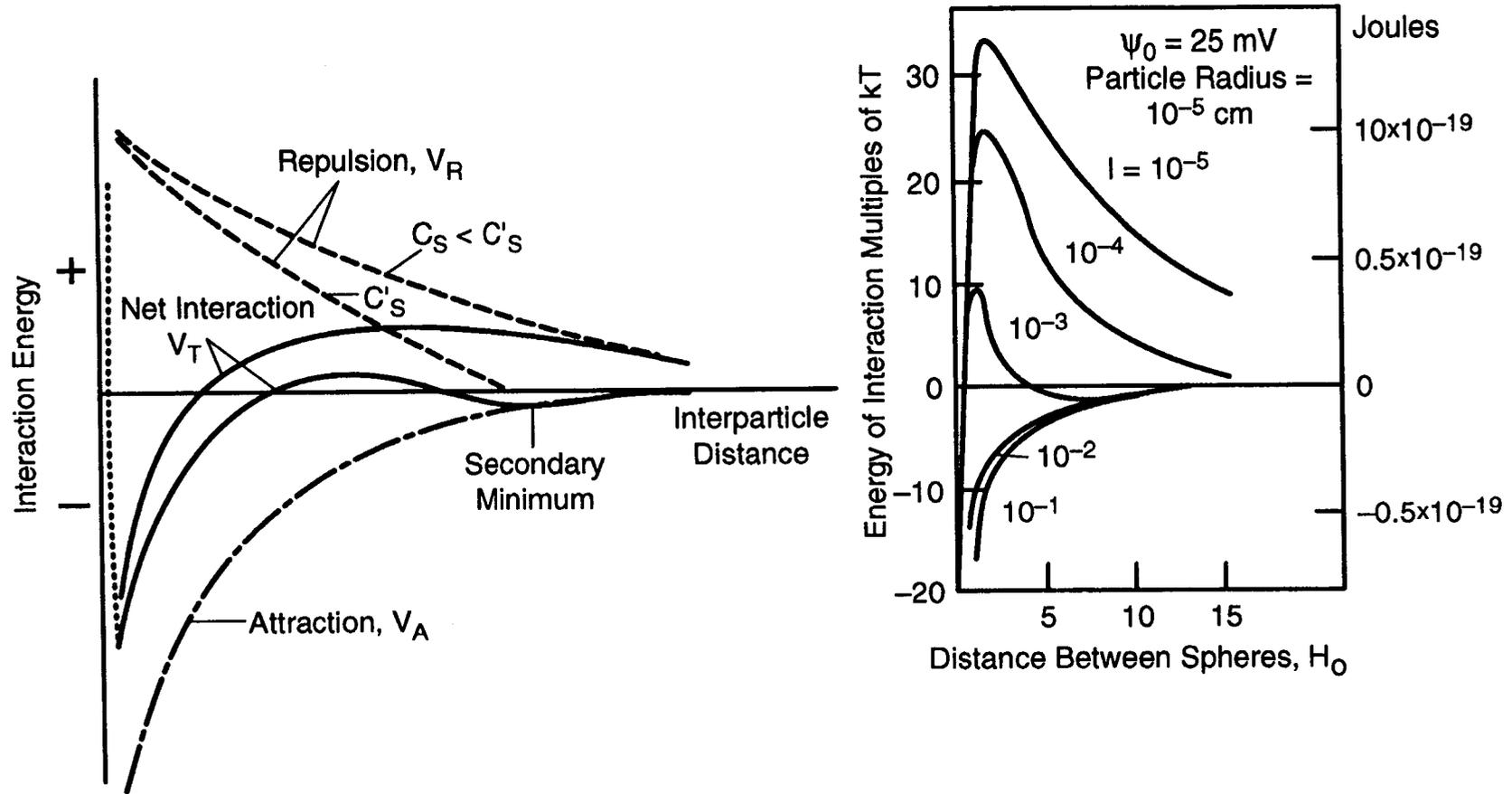


Figure 5-2. (a) Schematic curves showing the interaction energies between two charged particles: V_R = electrostatic repulsion, V_A = van der Waals Attraction, V_T = total net attraction, C_s = electrolyte concentration, C'_s = critical electrolyte concentration to allow coagulation; and (b) net interaction energies for constant potential spheres in solutions of different ionic strengths (I): Ψ_0 = electrostatic potential (adapted from Stumm and Morgan, 1981)

greater than that of the water. In general, this effect, called hydrodynamic chromatography (de Marsily, 1986; Hunter, 1987), 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). Another process leading to enhanced colloid transport is volume exclusion and/or charge exclusion. In this case, the colloid is excluded from diffusing into small dead-end pores by its size or through electrostatic repulsion. This enables the particle to remain in the advective flow path, resulting in faster transport to the accessible environment.

5.4 MATHEMATICAL TREATMENT OF COLLOID TRANSPORT

There is considerable debate among the waste management technical community with regards to the potential role and significance of colloids as a means to facilitate and accelerate the transport of radionuclides at repository sites. For example, Vilks (1994) concluded that the concentration of colloids in groundwaters at the Whiteshell Research Area in Canada was not sufficiently high for transport of radiocolloids to have a significant adverse impact on the release of radionuclides. Conversely, McCarthy and Zachara (1989) and McCarthy and Degueudre (1993) state that a low concentration of colloids in groundwaters at disposal sites should not be considered sufficient evidence for discarding the possibility of enhanced contaminant transport in colloidal form. These authors argue that low colloid concentrations tend to increase the stability of colloidal suspensions, thus allowing colloids to be transported more readily. The lack of a definitive colloid transport predictive capability and the lack of relevant laboratory and site-specific data on the presence, concentration, radioactivity, mobility, and properties of colloids fuels the debate because it prevents the systematic analysis of colloid transport as a potentially fast vehicle for radionuclide releases to the accessible environment.

Colloid mobility depends on two primary factors: (i) the stability of the colloidal suspension, and (ii) the interactions between the colloids themselves and between colloids and the walls of the channel through which the colloids are transported. The former governs the ability of colloids to remain suspended and thus their availability for transport, whereas the latter determines the rate at which colloids are transported in a flowing medium, the rate at which they can be captured by the walls of the channel or filtered, and the rate at which they are released to the accessible environment. The stability of colloidal suspensions was already discussed in Section 5.2. In this section, the discussion focuses on the phenomena that affects colloid–colloid and colloid–flow channel interactions.

Colloids can interact among themselves and with the walls of the channel bounding the flow and be captured, released, or filtered due to 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.

For colloids to travel more or less unimpeded through a porous medium, the diameter of the pores through which the colloids move must be significantly larger than the diameter of the colloids—at least 20 times larger (Section 5.3). Furthermore, because interactions between colloids and the walls of the flow channel are dominated by very small-range forces, the curvature of the pore walls have little

effect on the interactions. Therefore, neglecting the curvature of the pore walls and considering the pores as either parallel-plate or cylindrical channels is a common and typically good approximation when modeling colloid transport (Guzy et al., 1983). This approximation is employed in the discussion in this section and in Section 5.5.

It is well documented in the literature that colloid transport in a closed conduit, such as a parallel-plate channel, 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 as shown in Figure 5-3. 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 interactive forces dominate and the colloids may not be readily available for transport. As colloids in Region II could be 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 typically are not included in the calculation because they generally 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.

The objective of this section is to discuss the mechanistic phenomena that affect the mobility of colloids in Region II of Figure 5-3. An understanding of such phenomena is necessary in order to gain insights that may eventually permit the elucidation of the colloid transport impacts on radionuclide releases at an HLW repository site. McCarthy and Zachara (1989) and McCarthy and Degueldre (1993) both list the lack of such an understanding as one of the reasons for the absence of a colloid transport model at the present.

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 they are to gravitational settling, and, consequently, 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 forces associated with electrostatic, dispersion, Brownian motion, and hydrodynamic phenomena. Other factors are also significant contributors to the probability of successful colloid-colloid collisions. These factors are: the concentration of colloids, the chemistry of the system, and the temperature of the system. The effect of the chemistry of the suspension is expected to be very complex, and, therefore, it would not be prudent to speculate on its specific effect on colloid-colloid collisions. On the other hand, it can be qualitatively stated that the general tendency of increased colloid concentration and higher temperature is to increase interparticle collisions, thus increasing the number of successful collisions.

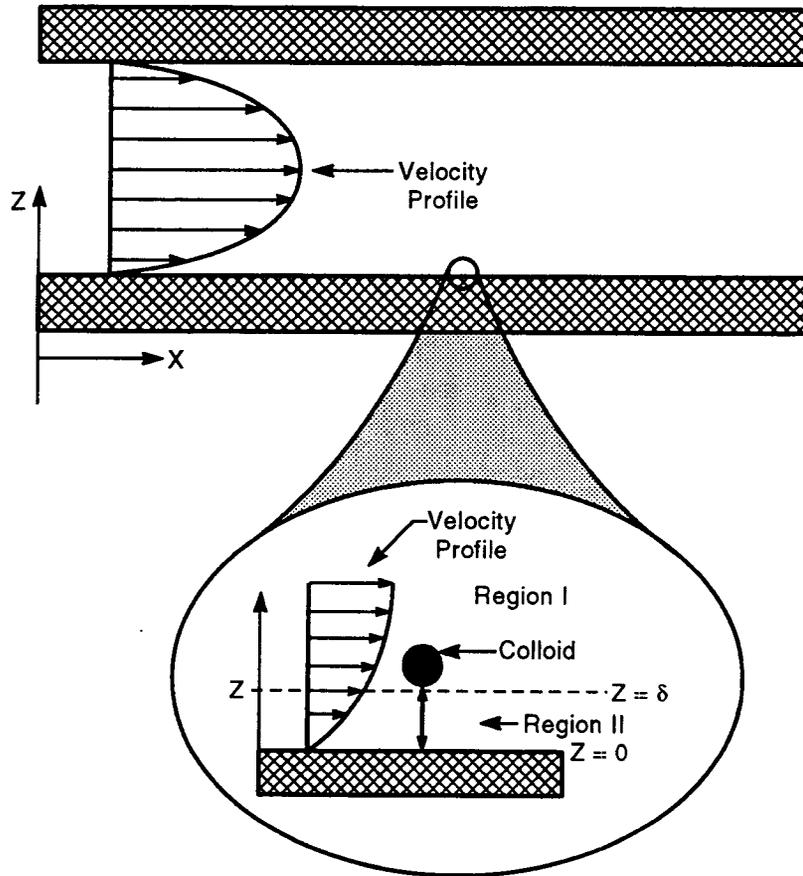


Figure 5-3. Schematic representation of convection (Region I) and attachment (Region II) regions that influence determination of average colloid-front velocity (adapted from van der Lee et al., 1993)

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 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:

$$\Phi_i = \frac{1}{2} \sum_{j=1}^{i-1} K_{i-j,j} N_{i-j} N_j - N_i \sum_{j=1}^{\infty} K_{ij} N_j \quad (5-4)$$

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. These external forces are primarily responsible for the movement of colloids from Region I to Region II in Figure 5-4 and their capture once they are within Region II. As will be demonstrated, the sum of these external forces could be used to estimate the rate at which colloids move vertically towards the walls of the channel.

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

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

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):

$$F_E = \frac{\epsilon_d \tau (\phi_c^2 + \phi_w^2)}{2} \left[\frac{g(H, \tau)}{f_z(H)} - \frac{g(H_u - H, \tau)}{f_z(H_u - H)} \right] \quad (5-6)$$

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

$$\kappa = \left[\frac{4\pi e^2}{\epsilon_d kT} \sum_{j=1} c_j Z_j^2 \right]^{\frac{1}{2}} \quad (5-7)$$

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 (5-6) 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):

$$g(H, \tau) = \left[\frac{2\phi_c \phi_w}{(\phi_c^2 + \phi_w^2)} - e^{-\tau H} \right] \frac{e^{-\tau H}}{1 - e^{-2\tau H}} \quad (5-8)$$

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. (5-6) 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

$$H = \frac{b}{a} + \frac{z}{a} - 1 \quad (5-9)$$

and

$$H_u = \frac{b}{a} - \frac{z}{a} - 1 \quad (5-10)$$

where

b = half-width aperture of the channel
 z = is the position from the bottom wall of the channel (Figure 5-4)

However, it should also be noted that the function $g(H, \tau)$ in Eq. (5-6) and the function $f(H, \eta)$, included in Eq. (5-11) below, decrease rapidly as the separation from a wall, H , increases. Therefore, in Eq. (5-6)

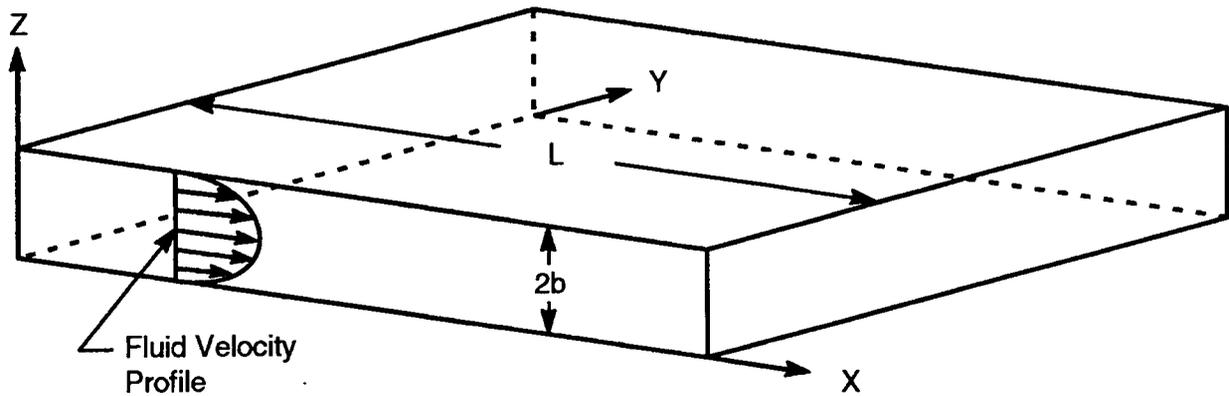


Figure 5-4. Schematic of parallel-plate channel

and in Eq. (5-11), 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

$$F_L = - \frac{2}{3} \frac{A}{a} \left[\frac{f(H, \eta)}{f_z(H)} - \frac{f(H_u - H, \eta)}{f_z(H_u - H)} \right] \quad (5-11)$$

where

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

$$f(H, \eta) = \{ [1 + 0.620725L + 0.07519L^2] [H^2(2 + H^2)] \}^{-1} \quad (5-12)$$

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

$$f(H,\eta) = \frac{[1.024172/L - 0.714228/L^2 + 0.555262/L^3]}{[H^2(2 + h)^2]} \quad (5-13)$$

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

Equations (5-5), (5-6), and (5-11) can be added to arrive at the sum of all the external forces acting on the colloids (Adamczyk and van de Ven, 1981)

$$F_{\text{ext}} = F_G + F_E + F_L \quad (5-14)$$

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

$$v_z = \frac{F_{\text{ext}}}{6\pi\mu a f_z(H)} \quad (5-15)$$

In Section 5.5.3, it will be shown how this vertical velocity can be included into the colloid transport equation. The term v_z could also be used to estimate the rate of colloid capture due to the external forces.

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, 1975; 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 $< 1 \mu\text{m}$ (Sections 2, 3, and 4). Therefore, an analysis of colloid transport should consider particle attachment to, and detachment from, the walls of the channel due to Brownian motion.

The colloidal-wall interactions due to Brownian motion are characterized by a potential energy function (Dahneke, 1975) (Figure 5-2). The total energy of a colloid under Brownian motion is

$$E_T = \frac{1}{2}mu^2 + E(H) \quad (5-16)$$

where

$$\begin{aligned} E_T &= \text{total energy} \\ m &= \text{mass} \\ u &= \text{velocity} \end{aligned}$$

The first term in the right-hand side of Eq. (5-16) 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 $H=H_{\min}$. In Part b of Figure 5-2, H_{\min} and H_{\max} are shown as the distance where the energy of interaction falls to $-\infty$ near the solid wall and the distance where the energy of interaction is maximum, respectively. 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 Smoluchowski'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.

$$\sigma_{\text{rel}} = D_B H_{\max} \left(\frac{e_{\max} e_{\min}}{2\pi kT} \right)^{\frac{1}{2}} \exp \left\{ - \left(\frac{E_{\max} - E_{\min}}{kT} \right) \right\} \quad (5-17)$$

and

$$\sigma_{\text{dep}} = D_B H_{\max} \left(\frac{e_{\max}}{2\pi kT} \right)^{\frac{1}{2}} \exp \left(- \frac{E_{\max}}{kT} \right) \quad (5-18)$$

where

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

In order to use Eqs. (5-17) and (5-18), the potential energy must be expressed in terms of H . Several papers in the literature have proposed such expressions (Dahneke, 1975; 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. It is fair to say that modeling the coupled transport of radionuclides in colloidal form and as dissolved species has not met with success. As a result, there is no predictive capability at present that would be suitable for PA analysis. This is not to say that attempts have not been made. In Section 5.1, nearly 20 different colloid transport modeling studies over the last 14 yr were referenced. That list is by no means complete; nevertheless, a review of such studies provides a fairly reliable snapshot of the current state-of-the-art in the development of colloid transport models for radioactive waste disposal sites. Studies that have modeled colloid transport for PA purposes have represented the colloid-capture term as either a sink term or death term; however, no expressions are provided for such terms (Nuttall et al. 1984, 1991; Grinrod and Cooper, 1993). Others (Bonano and Beyeler, 1985, 1987) approached the colloid transport problem from a more mechanistic perspective. In these studies, a rate for colloid capture

has been estimated, but the colloid transport model has not been coupled to a dissolved-species transport model. McCarthy and Zachara (1989) suggested that colloid capture could be simulated using a distribution coefficient concept, while Vilks (1994) contemplated the use of an effective colloid retardation factor. These authors did not discuss how the distribution coefficient or the effective retardation factor could be estimated. Thus, it is clear that the development of a mechanistic model coupling colloid and dissolved-species transport is a necessary first step towards the eventual development of a colloid transport model for PA analysis purposes. Whether or not a PA colloid transport model can be developed is unknown at present. It should be understood that modeling the simultaneous transport of colloids and dissolved species could be a formidable "bookkeeping" problem because of the need to track many different types of colloids and of dissolved species and the changes from one type of colloid to another. The problem could be an intractable one from a computational point of view.

These difficulties notwithstanding, the need exists to examine the coupled colloid-dissolved species transport problem from fundamental principles in order to gain necessary insights that could permit the resolution of some of the issues highlighted earlier. It may be possible to bound the problem so that a tractable model could be developed for use in PA analyses. It is noted that the discussion presented in the remainder of this section is advocated as neither the best nor the only modeling approach for coupled colloid-dissolved species transport. Rather, it is presented as a possible framework for gaining a fundamental understanding of the potential significance of colloid transport. The mechanistic approach employed in the discussion is consistent with the overall hierarchy of model development discussed by Park et al. (1994) that eventually results in models suitable for PA analysis.

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 in this section, 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). These assumptions can be considered to be conservative. The lack of flocculation tends to enhance the stability of the colloidal suspension thus making colloids more readily available for transport. If colloids extract momentum from the flow, the tendency is for the flow velocity to decrease; hence, the colloids will have a higher likelihood of settling out. Therefore, by assuming that the colloids do not extract momentum from the flow, the transport of the colloids is enhanced. 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 5-4. These simplifying assumptions notwithstanding, the set of transport equations that will be developed in the following 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

$$\frac{\partial(C_D\theta)}{\partial t} + q_x \frac{\partial C_D}{\partial x} = \theta D_x \frac{\partial^2 C_D}{\partial x^2} - \theta \lambda C_D - \theta M_{D-S} - \theta M_{D-C} - \theta M_{MD} \quad (5-19)$$

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, or it could be the rate at which the dissolved species sorbs onto a foreign colloid [Eq. (5-25)]. In either case, it provides the coupling between the transport equation for the dissolved species and the colloid transport equation [Eq. (5-23)].

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):

$$\frac{\partial[\rho_R G S_w (1 - \phi)]}{\partial t} = \theta M_{D-S} - \lambda \rho_R G S_w (1 - \phi) \quad (5-20)$$

Equation (5-20) 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

$$\rho_R (1 - \phi) S_w k_d \frac{\partial C_D}{\partial t} = \theta M_{D-S} - \lambda \rho_R k_d C_D S_w (1 - \phi) \quad (5-21)$$

where

- ρ_R = density of the rock
- k_d = distribution coefficient

- S_w = water saturation ($=\theta/\phi$)
 ϕ = porosity of the rock

Equations (5-19) and (5-21) are combined by linear superposition to give the transport equation for the dissolved species:

$$\frac{\partial C_D}{\partial t} + \frac{v_f}{R_d} \frac{\partial C_D}{\partial x} = \frac{D_x}{R_d} \frac{\partial^2 C_D}{\partial x^2} - \lambda C_D - \frac{M_{D-C}}{R_d} - \frac{M_{MD}}{R_d} \quad (5-22)$$

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), the effect of surface interactions between the colloids and the walls of the channel (Nuttall et al., 1991; Castaing, 1991; Hwang et al., 1990), or have a yet-to-be-defined coupling term (Grinrod and Cooper, 1993). 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. It is noted, however, that this model is provided here for discussion purposes only. This model has not been utilized in any specific studies. Furthermore, neither is it implied by the discussion that the data exist for inferring the numerical value of the parameters in the model. Rather, it is presented as a possible starting point for a preliminary assessment of colloid transport.

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

$$\begin{aligned} \theta \frac{\partial N}{\partial t} + \theta v_f \left[3 \left(\frac{z}{b} \right) F_2 - 1.5 \left(\frac{z}{b} \right)^2 F_1 \right] \frac{\partial N}{\partial x} + \theta \frac{\partial (v_z N)}{\partial z} \\ = \theta D_B \frac{\partial}{\partial z} \left(\frac{1}{\alpha} \frac{\partial N}{\partial z} \right) - \theta M_c + \theta M_r + S_c \end{aligned} \quad (5-23)$$

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. (5-15)

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. (5-17) and (5-18), while S_c can include such phenomena as nucleation, which was discussed earlier, or sorption onto a foreign colloid [see Eq. (5-25)].

The term $v_f [3(z/b) F_2 - 1.5(z/b)^2 F_1]$ in Eq. (5-23) 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 components needed to determine if colloid transport can enhance radionuclide releases to the accessible environment, the other component 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

$$C_C = N \rho_{RN} V_C \quad (5-24)$$

where

C_C	=	concentration
ρ_{RN}	=	density of the radionuclide
V_C	=	volume of the colloid

In this case, S_c in Eq. (5-23) 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

$$\frac{dC_C}{dt} = M_{D-C} \quad (5-25)$$

where

M_{D-C}	=	function of both N and the surface area of a colloid, A_c
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If the linear isotherm assumption were to be adequate, $C_C = k_d C_D$, Eq. (5-25) becomes

$$k_{dc} \frac{dC_D}{dt} = M_{D-C} \quad (5-26)$$

where

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

In this case, Eq. (5-26) can be substituted into the transport equation for the dissolved species, Eq. (5-22), and the latter becomes

$$R_{dc} \frac{\partial C_D}{\partial t} + \frac{v_f}{R_d} \frac{\partial C_D}{\partial x} = \frac{D_x}{R_d} \frac{\partial^2 C_D}{\partial x^2} - \lambda C_D - \frac{M_{MD}}{R_d} \quad (5-27)$$

where

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

However, there is no known evidence to support the assumption that the sorption of radionuclides onto naturally occurring colloids can be described by a linear isotherm.

5.5.4 Population Balance for Captured Colloids

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

$$\frac{dN_C}{dt} = M_C - M_R \quad (5-28)$$

where

N_C = number concentration of captured colloids
 M_C = rate of capture
 M_R = rate of release

Equation (5-28) 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 rate of capture, M_C , could be estimated from the solution of Eq. (5-23) as was done by Bonano and Beyeler (1985, 1987). The rate of release, M_R , could be estimated from Eq. (5-17). The mass of radionuclides contained by the captured colloids can be calculated either with Eq. (5-24) in the case of true colloids or with Eq. (5-25) for pseudocolloids.

5.6 LIMITATIONS OF CURRENT COLLOID TRANSPORT MODELS

The discussion in Section 5.5 demonstrated that, in principle, a coupled colloid-dissolved species transport model can be developed from a purely mechanistic perspective. This model, even though it is not devoid of simplifying assumptions, relaxes some key restrictions in existing models (e.g., the rate of colloid capture can be estimated from fundamental principles). Such a model could be used to perform systematic auxiliary analyses that will identify key processes and parameters dominating the transport of colloids. The results from such analyses could be used to simplify the model.

The model discussed in Section 5.5 may provide some improvements over existing models; however, there are a number of issues that are unresolved and that, more than likely, could prevent the defensible implementation of the model in PA analysis. First, data relevant to groundwaters at the candidate HLW disposal site needed to infer the values of the numerical parameters in the model are not available. Expert judgments could be used to obtain preliminary bounding values for the model parameters and determine those sensitive parameters which require detailed investigation. Second, there is a need to bound the colloid transport problem (i.e., reduce the number of colloidal species and dissolved species that need to be considered) so that the solution to the problem can be tractably implemented in PA analyses. If all possible radioactive colloidal species and dissolved species are considered in a fully coupled manner, the magnitude of the problem could be so formidable that it would tax the capacity of even the most advanced computers. Therefore, it is desirable to reduce the magnitude of the problem by identifying and concentrating on the colloidal species of potentially greater significance. Third, the uptake of radionuclides onto naturally occurring colloids should be investigated. There is uncertainty regarding the phenomena by which such uptake will take place [e.g., it has been suggested that sorption described using a linear isotherm could be used (McCarthy and Zachara, 1989)], but there are no data to support this suggestion. A concurrent investigation is needed that examines the formation of real radiocolloids due to homogeneous nucleation, precipitation, etc. Both of these studies should elucidate the uncertainty associated with the amount of radionuclides that can be transported by colloids relative to the amount transported as dissolved species, which would be a key component to determining the role and significance of colloids to radionuclide transport. Fourth, the stability of colloidal suspensions under conditions representative of groundwaters at the candidate HLW repository site is unknown. Determining the potential stability of the colloidal suspensions under relevant physico-chemical conditions is important to establishing the concentration of colloids available for transport. There is concern (McCarthy and Degueudre, 1993) that colloids are dislodged from the immobile rock matrix during sampling and that the apparent measured concentration of suspended colloids is higher than in reality. Fifth, there is uncertainty on how the presence of captured colloids on the surface of the immobile rock matrix could modify the latter's properties to prevent or decrease the capture of more colloids. For example, if colloids attach preferentially to specific sites at the immobile rock matrix, then such sites would become unavailable for future colloid capture. As the number of available capture sites decreases, the rate of colloid capture effectively decreases. This and other modifications to the surface properties of the immobile rock matrix due to the presence of captured colloids should be investigated.

6 SUMMARY AND RECOMMENDATIONS

This literature review resulted in several observations regarding the role that colloids can play in the estimation of a HLW repository long-term performance. These observations can be classified into three categories: (i) generic, (ii) Yucca Mountain site-specific, and (iii) KTU-related. For each of these categories, the observations can be further subdivided (e.g., subcategories of generic observations are colloid formation and colloid transport). Each of the general categories is addressed in more detail in the remainder of this chapter.

6.1 GENERIC OBSERVATIONS ON COLLOIDS

The motivation for this literature review arises from the uncertainty in the extent to which colloids can contribute to radionuclide releases to the accessible environment at a HLW repository site. There is considerable debate within the waste management community regarding the contribution of colloids to radionuclide releases. In the case of potential releases to the accessible environment from a HLW repository, failure to account for particulate transport of contaminants at waste sites may result in the underprediction of the extent of contaminant migration and overprediction of the time of arrival of the contaminants to the point-of-release. However, other studies have discarded colloids as a potentially important vehicle for contaminant transport due to low concentrations of colloids in groundwaters. Because construction and operation of a HLW repository may result in an increase in colloid formation, evaluations necessary to determine the significance of radionuclide release and transport by colloids are: (i) formation of radioactive colloids, and (ii) transport of radionuclides via colloids.

Besides the presence of naturally occurring groundwater colloids, several other processes can be identified as possible sources of colloids at a HLW repository. These processes include: leaching of vitrified wastefoms and spent fuel, corrosion of the EBS (mainly waste package and backfill, if used), interactions with other human-introduced materials used during construction and operation of the repository, and precipitation and disintegration processes. In addition, colloids may be generated by the interaction between radionuclides in suspension and exposed geologic media. The process of colloid generation 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 a variety of chemical conditions (e.g., Eh, pH, groundwater composition, etc.). Formation of colloids in the groundwater would be generally favorable for actinides because of solubility constraints. 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.

A main characteristic distinguishing colloid transport from the transport of dissolved species is size. While size is important, a variety of other phenomena and forces, the consideration of which is not necessary for dissolved-species transport analyses, also affects colloid transport. These phenomena and forces include: (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 of these phenomena and forces determine the interactions between colloids and between the colloids and the immobile geologic media. These interactions, in turn, govern the stability of colloidal suspensions and the rate of transport of colloids in stable suspensions.

Uncertainty in (i) the parameters and geochemical properties governing these phenomena and forces, and (ii) the source of colloids, have precluded the development of a transport model adequate for

PA calculations that include colloid transport. Some attempts have been made to develop such models; source/sink terms or retardation-like terms have been used to account for colloid-colloid and colloid-geologic media interactions. However, no explicit expressions for these terms have been provided; instead the terms are usually treated as adjustable parameters. In this study a mechanistic approach for modeling colloid transport was presented, but it cannot be legitimately claimed that the model presented in this report is appropriate for PA calculations for at least two reasons: (i) it is not clear that the parameters contained in the model can be successfully measured in either laboratory or large-scale experiments, and (ii) it is uncertain whether the mechanistic model can be reduced to one suitable for PA purposes.

It is possible to conduct systematic studies using the current state of knowledge to gain valuable insights about phenomena and parameters governing colloid generation and transport at HLW repository sites. These insights could form the basis for more focused investigations leading to the resolution of the aforementioned issues.

6.2 YUCCA MOUNTAIN SITE-SPECIFIC OBSERVATIONS

Field studies in the vicinity of the YM site demonstrate that natural inorganic and organic colloids and organic matter are present in significant amounts under some conditions. Natural heterogeneities and difficulties in field sampling for colloids, however, make it difficult to unambiguously determine the amounts of colloids present in the subsurface. Many of these particles are sorptive (clays, oxyhydroxides), but factors that control transport of radionuclides such as the stability of the colloid suspension and the sorption behavior of the actinides are strongly affected by changes in chemical conditions, including pH and ionic strength. For example, suspension stability may decrease under low pH conditions due to electrostatic attraction; under the same conditions, however, actinide sorption on oxyhydroxide phases is likely to be low.

Based on results reported in the available literature, it may be possible for colloids to form in the YM environment, but the extent to which they could contribute to overall radionuclide transport remains unclear. Preliminary porosimetry data at YM (U.S. Department of Energy, 1988) suggest that much of the matrix porosity is too small ($<10^{-7}$ m in diameter) to allow significant matrix transport of colloids but the fracture apertures are large enough to allow colloid transport. Mathematical models currently exist that can simulate colloid formation and transport for idealized systems (Nuttal, Jain, and Fertelli, 1991). However, these models typically rely on a number of 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 the chemical effects on sorption (Allison et al., 1991) dependence, but they have not been modified to consider colloid transport.

Most of the available information on colloid transport is for saturated zone hydrology. It is still uncertain to what degree understanding of colloid transport in the hydrologically saturated zone can be applied to represent 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 this need.

6.3 COLLOID-RELATED KEY TECHNICAL UNCERTAINTIES

In Section 1.5.1 of this report, 10 KTUs related directly or indirectly to colloid formation and transport were listed. It is the conclusion and recommendation of this study that the DOE should plan and undertake site characterization activities aimed at resolving these KTUs.

The evidence to date indicates that colloid transport could be important; however, a systematic analysis to determine the relative importance of colloid transport has yet to be conducted. Whether colloids represent a potentially important means for transport of radionuclides in the YM environment, in comparison to transport as dissolved species, is still uncertain. Based on the literature reviewed in this study, additional investigations may be necessary to obtain data under unsaturated conditions typical of YM that would increase confidence in assumptions made in current models, and for developing suitable PA models. Areas requiring additional information or data under typical YM conditions may include but are not necessarily limited to:

- Conditions for colloid stability (e.g., size and surface charge of colloids, ionic strength, and pH of solution)
- Formation kinetics of colloids (both geologic materials and wastefoms)
- Influence of container and waste package corrosion products and other human-introduced materials on formation and stability of colloids
- Colloid sorption and transport through partially fractured host rock under unsaturated repository conditions

The uncertainty associated with predicting the generation and transport rates of radioactive colloids and the failure to account for colloid transport in PA could lead to underestimation of radionuclide releases to the environment. Therefore, the NRC should independently undertake confirmatory studies addressing some of the concerns outlined in the colloid-related KTUs. There is a significant potential for impact of colloids on the evaluation of repository performance. Currently, no acceptable methodology for determining and demonstrating compliance with the regulations is available.

Specifically, to develop the independent capability necessary to review those aspects of the License Application (LA) related to colloid formation and transport, it is recommended that the NRC should focus on the following concerns related to the KTUs mentioned earlier.

- Uncertainty in identifying geochemical conditions that would influence particulate and colloid formation
- Understanding the effects of degree of hydrologic saturation on geochemical processes such as radionuclide sorption, precipitation, and formation of particulates, colloids and complexes, and their transport
- Parametric representation of retardation processes involving radionuclide-bearing particulates, colloids, and complexes

This evaluation can be accomplished through a combination of laboratory and field studies, PA modeling, and natural analog research.

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